

EMISSION AND CAPTURE PROCESSES IN GOLD AND SULFUR DOPED SILICON

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OLOF ENGSTRÖM

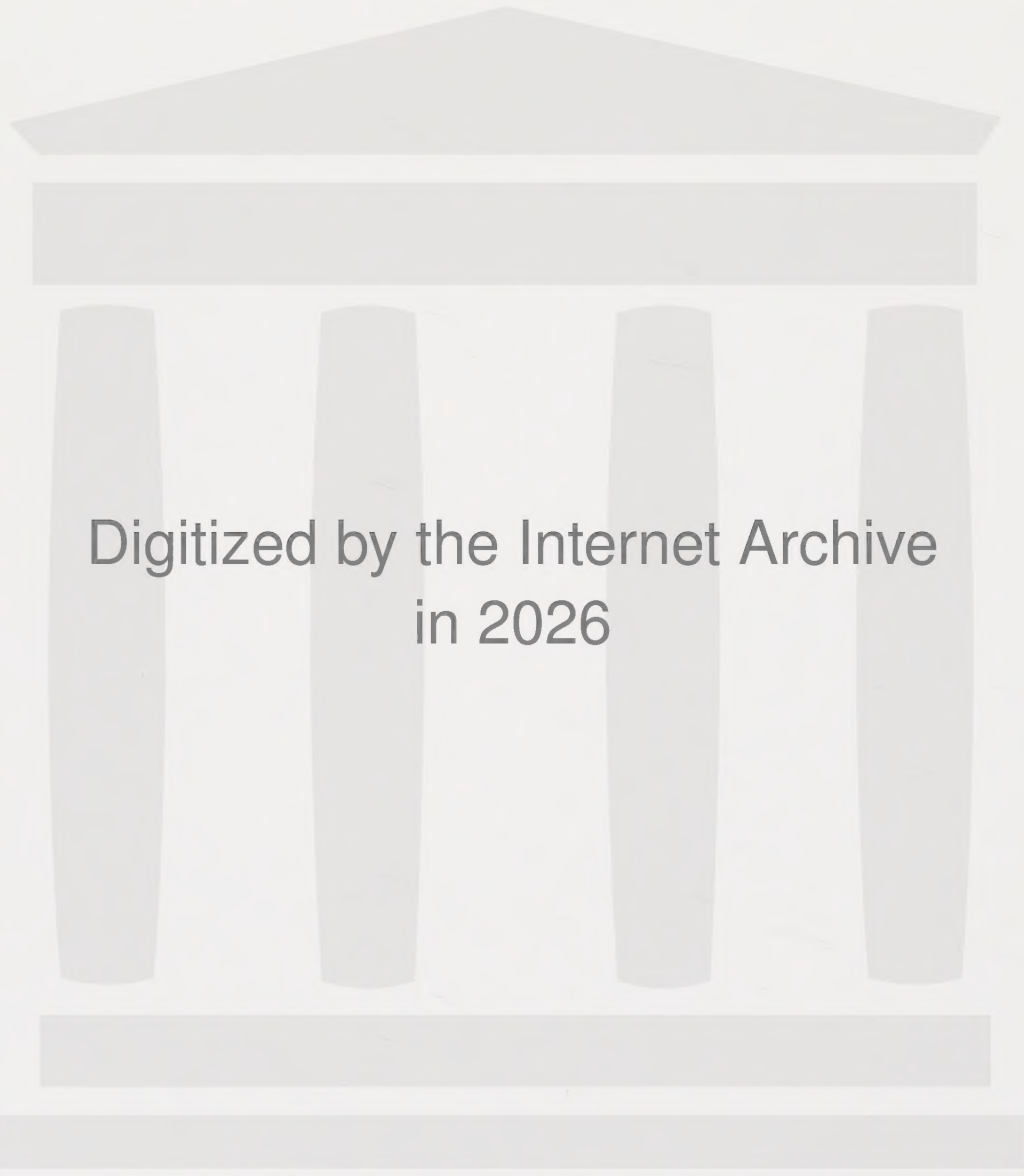


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I. INTRODUCTION

The main reason for the enormous importance of semiconductors in our time is the possibility of introducing foreign atoms into the crystal lattice in a controllable and reproducible way. Such "impurity-atoms" or "-centers" are traditionally divided into two classes, those which introduce shallow energy levels into the forbidden energy gap and those which introduce deep energy levels. The first kind determines the stationary electrical conductivity properties of the crystal, while the second kind determines the transient conductivity behaviour. Gold and sulfur impurities in silicon crystals belong to the latter class.

In the Western cultural hemisphere, gold and sulfur are considered as two most mythical elements. Gold is often distinguished as a heavenly material, while sulfur is normally associated with Hell. Even though, in accordance with this dissimilarity, the two elements also exhibit quite different behaviour when used as dopants in silicon, it has

never come into the author's mind that their properties as deep impurity centers would be impossible to observe and explain with rational methods. Looking at the history of science, one finds that methods of attacking scientific problems have more and more become liberated from metaphysical associations and it is the author's hope that he has taken part in this tradition.

This thesis contains four papers about the thermal and optical properties of gold doped and sulfur doped silicon:

- I) Temperature dependence of the gold acceptor energy level in silicon
[Applied Physics Letters 25, 413 (1974)]
- II) Thermal activation energy of the gold acceptor level in silicon
[Journal of Applied Physics 46, 831 (1975)]
- III) The role of displacement currents in deep impurity induced PN-junction transients
[Preprint]
- IV) Optical properties of sulfur doped silicon
[Preprint]

The work in all papers was carried out in collaboration with professor Hermann G Grimmeiss. In paper III, Dr Stellan Braun was also a co-author.

Before turning to the papers, a brief survey of the field of deep

semiconductor impurities in general and gold and sulfur impurities in particular will be given, to point out where this work fits into the huge pattern of results in semiconductor physics. In section II, the influence of deep energy levels on technical problems is discussed, ways of formulating and solving electronic state problems are sketched and definitions of common quantities are given. The available measurement techniques for investigating deep impurity energy levels are reviewed in section III. Sections IV and V are concentrated on gold and sulfur as impurities in silicon and, finally, in section VI the contribution in this thesis is summarized.

II. DEEP IMPURITY CENTERS IN SEMICONDUCTORS

II.1 Technical importance

When a semiconductor is exposed to an external perturbation creating free charge carriers in its conduction and valence bands and the perturbation is suddenly removed, the carriers will revert back to their thermal equilibrium states by recombination. The time needed for this process is called the lifetime of the carriers and the recombination processes can be of mainly two different types (fig 1).

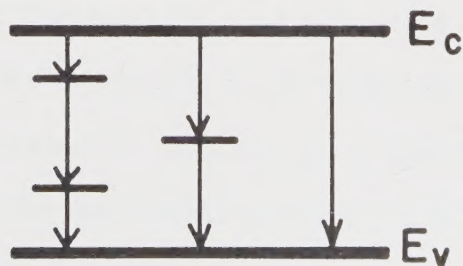


Fig. 1

Recombination can take place directly between an electron in the conduction band at energy E_c and a hole in the valence band at E_v , or it can go via energy levels in the band gap as step processes. By considering black-body radiation and the detailed balance principle of thermodynamics, it was shown about twenty years ago by van Roesbroeck and Shockley ¹⁾ that the direct processes have a very small probability of happening in such crystals as germanium and silicon. The theoretical lifetimes for carriers in intrinsic silicon can be estimated from their work to be about 4 hours. This value should be compared with measured lifetimes in the purest silicon commercially available today, which is in the region of 10^{-3} seconds. Step recombination processes via deep energy levels are the factor determining carrier lifetimes. This also means that carrier lifetimes in semiconductors can be controlled by doping with deep impurities and this is an important tool used in the fabrication of semiconductor junction devices, where switching speeds can be controlled by controlling the amount of excess carriers.

When a PN-junction is forward biased, excess carriers are injected into the neutral P- and N-regions. Switching the diode back to the reverse direction the junction does not bring up the voltage until the excess charges have disappeared. If no recombination can take place, the time needed for the device to function as a reverse biased diode would be the time needed for the excess carriers to be removed out to the contacts. If, however, deep impurities are present, the excess carriers disappear through fast recombination and the functional time of

the component is lowered. This is of great importance in for example the production of switching diodes and fast thyristors.

In materials with larger energy band gaps such as, for instance, gallium phosphide (2.3 eV), deep level recombination studies have become important due to the fact that in these materials visible light is created in the recombination process ²⁾. From these materials light emitting diodes are made. These are used as long-life visible indicators and display units.

Deep impurities also play an important part in photoconductive devices. These are normally made of CdS with a band gap of 2.4 eV corresponding to the region between green and blue in the visible spectrum. The spectral response and the sensitivity of these components are controlled by introducing deep energy levels in the energy band gap.

In the sixties many studies of space charge effects in bulk materials due to deep centers were initiated ³⁾. Negative differential resistance and oscillation phenomena were found in a large number of systems. So far, these effects have found a limited technical importance but might become of importance in the future.

II.2 Theoretical description of the impurity perturbation problem

The energy eigenvalue problem for electrons in a perfect crystal can be solved using the Schrödinger equation

$$\hat{H}^0 \psi^0 = E^0(k) \psi^0 \quad (1)$$

where the superscript denotes perfect-crystal quantities. The Hamiltonian is given by

$$\hat{H}^0 = -\frac{\hbar^2}{2m_0} \nabla^2 + V^0 \quad (2)$$

where V^0 is a periodic potential arising from the lattice built up by the regular arrangement of atoms. In a three-dimensional crystal, the relations are a bit more complicated due to the symmetry properties of the crystal. The purpose of this survey will, however, be satisfied by considering a chain of lattice points representing a one-dimensional crystal and the one-band equation (1).

Using periodic wave functions of the Bloch-type in eq (1),

$$\psi_k^0 = u_k(r) e^{ikr} \quad (3)$$

where k is the wave number and $u_k(r)$ is a periodic function with the period of the lattice, quasi-continuous bands of energy eigenvalues separated by forbidden energy regions are found. This is the familiar band model of crystals.

If now one of the crystal atoms is taken away and a foreign atom with different electronic properties is inserted, the crystal potential V^0 will be perturbed and the new potential V can be written

$$V = V^0 + U \quad (4)$$

where $U(r)$ is the perturbation potential created by the impurity atom.

The perturbed wave function ψ can be written as an expansion of an orthonormal set of Bloch-functions

$$\psi(r) = \sum_k F(k) \psi_k^0(r). \quad (5)$$

The problem of finding the electronic energy levels is now that of determining the eigenvalues of

$$(\hat{H}^0 + U) \psi = E(k) \psi. \quad (6)$$

By making a standard perturbation calculation, i.e. inserting eq (5) in (6), multiplying both sides with ψ_k^{0*} and integrating over all space,

$$\int \psi_k^{0*} (H^0 + U) \sum_k F(k) \psi_k^0 dv = \int \psi_k^{0*} E(k) \sum_k F(k) \psi_k^0 dv \quad (7)$$

one finds

$$E^0(k) F(k) + \sum_{k'} \langle \psi_k^0 | U | \psi_{k'}^0 \rangle F(k') = E(k) F(k). \quad (8)$$

At this point, to evaluate the matrix element $\langle \psi_k^0 | U | \psi_{k'}^0 \rangle$, detailed information about the form of the impurity potential U has to be used. If the potential is assumed to arise from a point charge coming from the ionized impurity so that $U(r)$ is a function which varies slowly compared to the lattice parameters and which does not contain high-order Fourier components, i.e. $U(r)$ is of the form

$$U(r) = - \frac{e^2}{\epsilon \epsilon_0 r} \quad (9)$$

equation (8) can be approximated by a Schrödinger equation of hydrogen type

$$- \left[\frac{\hbar^2}{2 m^*} \nabla^2 + \frac{e^2}{\epsilon \epsilon_0 r} \right] F(r) = E F(r) \quad (10)$$

where the electron mass is taken to be the effective mass m^* in the band. This is the idea of the so called Kohn-Luttinger Effective Mass

Theory (KL-EMT)⁴⁻⁶⁾. The eigenvalues obtained from equation (10)

$$E_n = \frac{1}{n^2} \frac{m^*}{2\hbar^2} \left(\frac{e^2}{\epsilon\epsilon_0} \right)^2 \quad (11)$$

are in good agreement energy values found for excited states of shallow impurities in germanium and silicon.

For deep impurities and for the ground states of shallow impurities, however, the potential approach of eq (9) can no longer be used in general. This is mainly because faster varying contributions to the potential from the impurity core and from the disturbed lattice appear in the central cell region. Here, the so called "isocoric" impurities seem to play an anomalous role. These are impurities belonging to the same row of the periodic table as the host atoms. They have thus similar electronic configurations in their core parts and therefore produce only small changes in the core potential when introduced into a crystal. In the case of silicon, the atoms of phosphorus and sulfur are isocoric and it seems that the latter can be described by KL-EMT despite the fact that sulfur is a deep impurity in silicon. This has been argued theoretically⁷⁾ and is experimentally confirmed by our optical investigations in paper IV.

For non-isocoric shallow impurities and deep impurities, other corrections which must be made are due to the breakdown of the usual screening approximation in the vicinity of the impurity ion, the need of including many bands in the expansion of perturbed wave functions and the overlap of wave functions from different valleys in the Brillouin-zone. Several attempts have been made to improve the theory of shallow impurities by taking such corrections into account⁹⁻¹⁵⁾ and to

describe deep impurities using various techniques¹⁶⁻²¹⁾. The first general description was recently given by Pantelides and Sah in ref 7 and 8 where pseudo-potential theory was used for non-isocoric impurities: this goes over into the KL-EMT approximation for the special case of isocoric impurities.

II.3 Carrier statistics at thermal emission and capture processes

The thermodynamical properties for the systems of electrons and holes in semiconductors were formulated early in the semiconductor history^{22,23)} and in 1952 the so-called "Shockley-Read-Hall" statistics were described^{24,25)} in two papers which have become classics. This theory describes emission - capture processes via a localized impurity in terms of life-time and emission and capture rates.

By applying the laws of thermodynamics to the system of a semiconductor containing a localized center capable of trapping at most one electron (fig 2), one finds for the mean number $\bar{r}$ of electrons trapped at a single center²⁶⁾

$$\bar{r} = \frac{1}{1 + \frac{g_0}{g_1} \exp \left(\frac{E_T - E_F}{kT} \right)} \quad (12)$$

where g_0 and g_1 are the degeneracies of the center with no electron and one electron captured respectively, E_T is the energy level associated with the center and E_F is the Fermi-level at thermal equilibrium.

We now introduce the notation $\epsilon_n^t(E)$ (fig 2), which represents the number of electrons emitted per second and center from the level E_T

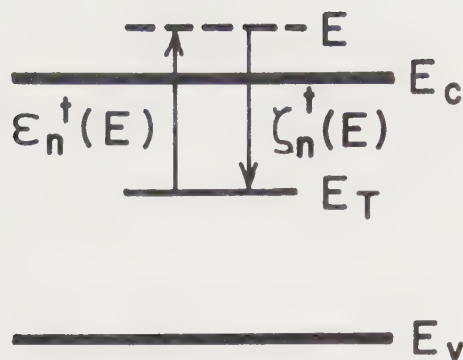


Fig.2

to a level E in the conduction band if the center contains one electron and level E is empty. Similarly, $\zeta_n^t(E)$ denotes the number of electrons captured per second and center if level E is filled by one electron and level E_T is empty. If the concentration of centers at E_T is N_{TT} , the total emission $dU_n^t(E)$ per second and unit volume from E_T to E is

$$dU_n^t(E) = \bar{r} N_{TT} \epsilon_n^t(E) (1-f(E)) N(E) dE \quad (13)$$

and for the capturing process $dR_n^t(E)$

$$dR_n^t(E) = (1 - \bar{r}) N_{TT} \zeta_n^t(E) f(E) N(E) dE \quad (14)$$

where $N(E)$ is the density of states in the conduction band and

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

is the Fermi-Dirac distribution.

The detailed balance principle requires that at thermal equilibrium $dU_n^t(E) = dR_n^t(E)$ and from eqs (13) and (14) the relation between ϵ_n^t and ζ_n^t is given by

$$\epsilon_n^t(E) = g \cdot \zeta_n^t(E) \exp\left(-\frac{E - E_F}{kT}\right) \quad (15)$$

where $g = g_0/g_1$ is the degeneracy factor of the center. The quantities ϵ_n^t and ζ_n^t are, however, theoretical quantities. Conversion to observable quantities is made by introducing the thermal emission rate e_n^t and the thermal capture rate c_n^t defined by

$$e_n^t = \int_{CB} \epsilon_n^t(E) N(E) (1-f(E)) dE \quad (16)$$

$$c_n^t = \frac{1}{n} \int_{CB} \zeta_n^t(E) N(E) f(E) dE \quad (17)$$

respectively. Next, by putting eq (15) into (16) and using (17) for identification, one finds

$$e_n^t = g \cdot c_n^t N_C e^{-\frac{E_C - E_T}{kT}} \quad (18)$$

where N_C is the effective density of states for the conduction band.

Analogous reasoning for hole excitation to the valence band gives

$$e_p^t = g^{-1} c_p^t N_V \cdot e^{-\frac{E_T - E_V}{kT}} \quad (19)$$

where e_p^t and c_p^t are now the thermal emission and capture rates for holes and N_V is the effective density of states for the valence band.

The measurement techniques used to obtain e_n^t , e_p^t , c_n^t and c_p^t are described in later sections.

The quantities ϵ_n^t and ζ_n^t are the bridges between statistical mechanics and quantum mechanics. Such a description might be made by putting

$$\epsilon_n^t(E) N(E) = \sigma_n^t(E) \cdot v^t(E) \cdot D^t(E) \quad (20)$$

where $\sigma_n^t(E)$ is the cross section for the excitation process, $v^t(E)$ is the velocity and $D^t(E)$ is the density of exciting particles. The cross section might in turn be expressed as

$$\sigma_n^t(E) = \text{const} \cdot \left| \langle f | \hat{H}^t | i \rangle \right|^2 N(E) \quad (21)$$

where ψ_f and ψ_i are the wave functions for the carrier in the band and at the impurity respectively, and $\hat{H}'$ is the perturbation Hamiltonian for interaction with the electron in the center.

By introducing emission and capture rates, a powerful tool for the description of recombination traffic at a localized center has been made available. If the number of trapped electrons and holes are denoted by n_T and p_T respectively, the time dependence of trapped electrons at the center when the semiconductor has been disturbed out of thermal equilibrium (fig 3)

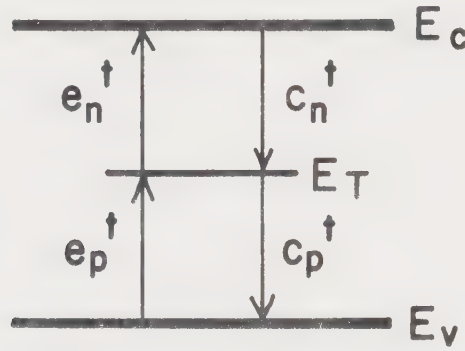


Fig.3

can be written

$$(R_n^t - U_n^t) - (R_p^t - U_p^t) = \frac{dn_T}{dt} = c_n^t n p_T - e_n^t n_T - c_p^t p n_T + e_p^t p_T \quad (22)$$

Here $n = n_0 + \delta n$ and $p = p_0 + \delta p$ are the free carriers in the bands, n_0 and p_0 are the equilibrium values and δn and δp are the perturbations. If the perturbation is small so that the quasi-Fermi level for the center is not changed it follows $\delta n = \delta p$, $dn_T/dt = 0$ and we may define a lifetime by

$$\tau = \frac{\delta n}{R_n^t - U_n^t} = \frac{\delta n}{R_p^t - U_p^t} \quad (23)$$

Substituting eqs (18) and (19) into (22) and (23) then gives

$$\tau = \frac{\tau_{p0}(n_0 + g n_1) + \tau_{n0}(p_0 + g^{-1} p_1)}{n_0 + p_0} \quad (24)$$

where

$$\tau_{n0} = \frac{1}{c_n^t N_{TT}} ; \quad \tau_{p0} = \frac{1}{c_p^t N_{TT}}$$

and

$$n_1 = N_c \exp\left(-\frac{E_c - E_T}{kT}\right) ; \quad p_1 = N_v \exp\left(-\frac{E_T - E_v}{kT}\right).$$

Statistics for multiply-charged centers have been obtained in refs 27-29 and a generalization of Shockley-Read-Hall statistics involving electron-electron interactions has been given by Landsberg in ref 30.

II.4 Non-radiative recombination

The importance of non-radiative recombination has been known for more than twenty years. Several hundred papers on the subject have been published ³¹⁾, but still many basic questions are unanswered. In an article by Haug ³²⁾ it is stated that non-radiative recombination "...erfolgt strahlungslos; es bleibt dunkel. Mit dieser Eigenschaft hat leider auch die Theorie dieser Übergänge manches gemein..."

Because this kind of transition cannot be observed directly, the parameter which is measured in experimental studies is the lifetime of carriers in the bands. If the impurity level is deep enough and the measurement is made on minority carriers, which is often but not always the case, one can see from eq (24) that

$$\tau = \tau_{p0} = \frac{1}{c_p^t N_{TT}} \quad (25)$$



for n-type samples and

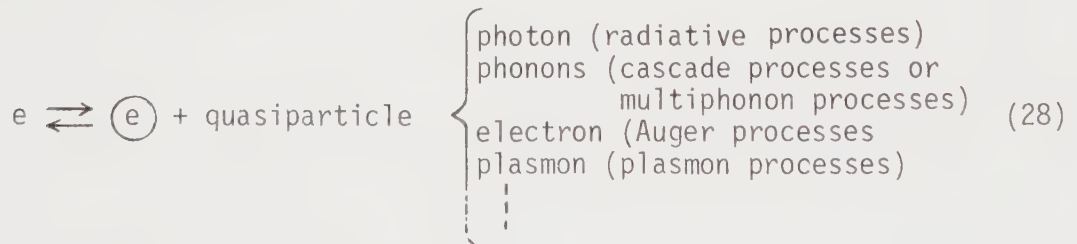
$$\tau = \tau_{no} = \frac{1}{c_n^t N_{TT}} \quad (26)$$

for p-type samples. The capture rates $c_{n,p}^t$ can in turn be expressed as

$$c_{n,p}^t = \langle v_{TH} \rangle_{n,p} S_{n,p}^t \quad (27)$$

where $\langle v_{TH} \rangle$ is the mean thermal velocity and S_n^t and S_p^t are the capture cross sections for carriers in the bands.

A large number of experimental investigations of capture cross sections for different impurities in germanium and silicon have been made ³⁾³³⁾³⁴⁾. The values for different systems vary in the enormous rate $10^{-22} - 10^{-12} \text{ cm}^2$. From this, it can be seen that the geometrical size of a center (10^{-16} cm^2) is not an adequate estimate for cross sections. This is due to the fact that an electron must not only come to the vicinity of the center but, once there, it must also perform the unlikely event of losing about 0.5 eV of energy. The recombination and excitation can schematically be described so that the energy released or supplied is carried by some quasi-particle created or annihilated in the process in the following way:



where e is a free carrier in the band and $\textcircled{e}$ is a bound carrier in the impurity. It seems that in Ge and Si ³³⁾ attractive centers have cross sections in the range larger than 10^{-15} cm^2 , neutral centers in the range $10^{-17} - 10^{-15} \text{ cm}^2$ and repulsive centers normally have cross

sections smaller than about 10^{-17} cm^2 . One way of distinguishing between different processes in expression (28) is to measure their temperature dependence. Large capture cross sections often have a temperature dependence of the form T^{-n} , where n varies between 0 and 4. These centers, which have been dubbed "giant traps" ³³⁾³⁴⁾ by Lax, are assumed to capture carriers through a phonon cascade process, where the carriers recombine through a ladder of excited states emitting a phonon at every step. This approach leads to large capture cross sections and negative temperature dependences. Attempts have been made ³⁶⁻³⁹⁾ to refine Lax's cascade theory, but the approximations are still so rough that the theoretical results must be assumed uncertain ³²⁾ by a factor of about 10. However, comparing experimental results by different authors, one also often here finds large discrepancies, in measurements made on one and the same system. This illustrates the complexity of the problem and cascade theory, even if rough, is the best way so far of explaining the behaviour of the "giant traps".

All other processes in expression (28) have smaller transition probabilities than cascade processes. In the case of multiphonon processes, the phonons are created by interaction between the impurity atom and the surrounding lattice ⁴⁰⁾. The temperature dependence of the capture cross section should then be characterized by an activation energy. This has been found for Ge:Cu ^{41,42)}, Ge:Ni ⁴³⁾ and in GaP and GaAs ⁶⁷⁾. For Ge:Cu it was, however, shown by Kalashnikov ⁴⁴⁾ that the temperature dependence could be more simply explained by taking into account the multilevel nature of the center using the statistics of Sah and Shockley ²⁹⁾. Multiphonon processes can be expected to have a greater importance in polar semiconductors where optical transitions are connected with Stokes-shift ²³⁾.

In an Auger process, one charge carrier from the conduction band is recombined to the impurity level and another carrier in the band is excited to a higher state in the band ⁴⁵⁾. The opposite is an impact ionization of the center and these two processes can therefore be connected by detailed balance considerations ⁴⁶⁾. Because Auger-recombination is based on interaction between free carriers, it is very sensitive to the carrier density and does not normally become important until the free carrier concentration exceeds about 10^{18} cm^{-3} . Similar relations are true for plasmon processes, where the energy is taken up by collective oscillations in the free carrier plasma ³²⁾.

II.5 Optical excitation

At thermal equilibrium, the optical emission and capture processes of an impurity can be described in terms of optical emission rates $e_{n,p}^0$ and optical capture rates $c_{n,p}^0$ and expressed in a formula similar to eq (23), simply by interchanging the superscripts t and o. If, however, the illumination comes from an external light source so that thermal equilibrium no longer holds, recombination does not necessarily appear optically but is determined by all possible mechanisms. If the temperature is assumed to be so low that the emission process is determined entirely by optical excitation, eq (23) must be written as

$$R - U^0 = \frac{dn_T}{dt} = c_n^t n p_T - e_n^0 n_T - c_p^t p n_T + e_p^0 p_T \quad (29)$$

As will be shown in section II.6, c_n^t and c_p^t are sums of capture rates belonging to all possible recombination mechanisms.

In analogy with eq (17), the optical emission rate for electrons can be written

$$e_n^0 = \int_{CB} \epsilon_n^0(E) N(E) (1-f(E)) dE \quad (30)$$

and the optical ionization cross section σ_n^0 can be defined by analogy with eq (21) as

$$\epsilon_n^0 \cdot N(E) = \sigma_n^0(E) \cdot I(E) \quad (31)$$

where $I(E)$ is the photon intensity distribution of the applied light.

Measurements are normally performed using a monochromator with a non-zero line-width ΔE , so, writing the photon flux $L(E')$ as

$$L(E') = I(E') \Delta E, \quad (32)$$

eq (30) and (31) give (for $f(E) \ll 1$)

$$\begin{aligned} e_n^0(E') &= \int_{CB} \sigma_n^0(E) I(E) (1-f(E)) dE \cong \sigma_n^0(E') I(E') \Delta E = \\ &= \sigma_n^0(E') L(E'). \end{aligned} \quad (33)$$

The optical emission rate is an observable quantity and can be made to yield the optical ionization cross section if the flux $L(E)$ is known. Theoretically, the ionization cross section can be calculated from the Fermi Golden Rule in analogy with eq (22):

$$\sigma_n^0 = \left(\frac{E_{eff}}{E_0} \right)^2 \left(\frac{\mu_0}{\epsilon \epsilon_0} \right)^{1/2} \cdot \frac{2h}{\nu A^2} \gamma \left| \langle f | \hat{H}' | i \rangle \right|^2 N(E) \quad (34)$$

Here E_{eff}/E_0 is the ratio between the optical electric field effective in inducing the transition, E_{eff} , and the average optical field in the crystal, E_0 . ϵ is the relative permittivity, ν is the frequency of the light and the perturbation Hamiltonian can be taken to be

$$\hat{H}' = - \frac{e}{m} \hat{p} \bar{A} \quad (35)$$

where $\bar{A}$ is the vector potential, $\hat{p}$ is the momentum operator and m the mass of the carrier. The matrix element in eq (34) is normally evaluated for the excitation of a one-particle system. When in practice a many-particle configuration is excited, the matrix element cannot be evaluated so long as the electron configuration of the impurity is not known. When using a one-particle matrix element, a factor γ should be inserted as shown in eq (34). It is normally difficult to find a proper value of γ . This is also the case for the effective field ratio E_{eff}/E_0 . The accuracy of a theoretical estimation of a photo ionization cross section therefore depends on the possibility of finding accurate values of these parameters. In applying eq (34), it is important to use as good approximations as possible for ψ_i, ψ_f and $N(E)$. The wave function ψ_i for an electron in the impurity is determined by the impurity potential. Many calculations using different ψ_f , impurity potentials and $N(E)$ are to be found in the literature ⁴⁸⁻⁵⁷).

II.6 Generalized formulation of emission and capture processes

In the literature about emission and capture processes, distinctions are made between thermal and optical processes in the same way as in section II.4 and II.5. In thermal measurements, it might be tempting to believe that the results are solely due to interactions between the charge carriers and phonons. This is not so. The thermal emission and capture processes are the results of any one of the interaction possibilities given in expression (28). To clarify what really is measured in a thermal investigation, a generalized consideration will be made in this subsection.

Let us first state that all quasiparticles in expression (28) are present in the semiconductor even at thermal equilibrium. Equations (21) and (31) can therefore be written in a generalized way as

$$\epsilon_n^i(E) N(E) = \sigma_n^i(E) I^i(E) \quad (36)$$

where i labels one of the possible interactions in expression (28) and $I^i(E)$ is the intensity distribution of the corresponding quasiparticle at thermal equilibrium. The total thermal emission probability, $\epsilon_n^t(E) N(E)$, from the impurity energy level to a level in the conduction band can thus be expressed as

$$\epsilon_n^t(E) N(E) = \sum_i \sigma_n^i(E) I^i(E) \quad (37)$$

where the sum is taken over all possible interaction processes. The detailed balance principle now requires that the number of quasiparticles created in a certain recombination process must be balanced by the number of quasiparticles annihilated in the corresponding excitation process, i e,

$$(1-f(E)) \bar{r} \sigma_n^i(E) I^i(E) = (1-\bar{r}) \tau_n^i(E) N(E) f(E). \quad (38)$$

By using eq (36) and reasoning analogous with that used in the deduction of eq (19), one finds

$$e_n^i = g N_c c_n^i e^{-\frac{E_c - E_T}{kT}} \quad (39)$$

The measured emission rate e_n^t is the sum of all possible interactions

$$e_n^t = \sum_i e_n^i = g N_c \cdot e^{-\frac{E_c - E_T}{kT}} \sum_i c_n^i \quad (40)$$

As will be described later in section III.2, the most usual method of measuring thermal emission rates is one in which the excitation process is made in a PN-junction. In this case, it is important to note that

the emission rates measured are results from the excitation of only those quasiparticles which are found in the space charge region. This means that, for instance, Auger-processes are ruled out and in these measurements preferentially phonon and photon processes are observed. When making explicit measurements of emission rates in PN-junctions and capture rates in neutral material, the results can be put into eq (40) only if Auger-recombination is negligible compared to other processes.

As can be seen, the terms "thermal emission" and "thermal capture" say nothing about the interaction mechanism. They are just measures of whichever mechanism is dominating at thermal equilibrium. The classification into "thermal" and "optical" processes is therefore not unique. A thermal process might be optical in the sense that it is generated mainly by photons. A more powerful classification is to distinguish between photon processes, phonon processes etc.

III. MEASUREMENT TECHNIQUES

III.1 Capture rates

As already mentioned above, recombination measurements in semiconductors have a comparatively long history and therefore a large number of methods has been developed to measure lifetimes and capture rates since the first investigations were made in 1951 (the so-called "Haynes-Shockley" experiment⁵⁸⁾). The methods can be divided into transient methods in which the lifetime is often established from a current decay and steady state methods in which the capture rates are calculated from measurements of diffusion lengths⁵⁹⁾.

In the photoconductivity decay methods, short pulses of light are used to introduce excess carriers, resulting in a change of conductivity of the sample. A lower limit to the lifetime resolution obtainable is set by the sharpness of the cut-off of the light pulses. In the early measurements, spark gaps, Kerr-cells and rotating mirrors were used to produce pulses giving resolutions of about 10^{-7} s. In a recent measurement on copper doped germanium⁶⁰⁾, a GaAs electro-optical modulator was used with a rise time of about 0.5 ns, giving a response time of 4 ns to the entire system. Photoconductivity methods are direct measurements of lifetimes, but the decay constant might be affected by surface recombination and trapping. Another common transient method consists of the electrical injection of carriers across a PN-junction followed by reversal of the polarity of the junction. This gives rise to a current transient in the reverse direction of the PN-junction, from measurement of which the lifetime can be obtained⁶¹⁻⁶³⁾.

The influence of surface recombination and competing trapping is avoided in the steady state method used in paper II of this thesis⁶⁴⁾. In this case, carriers are injected by illuminating a PN-junction diode with light. The light should have a photon energy high enough to be absorbed close to the surface, thus creating a very thin source of minority carriers. By measuring the reverse current created by the diffusion of minority carriers to the PN-junction, the diffusion length can be determined from a plot of current versus space charge region (see paper II). In this case, however, the mobility must be known in order to calculate the capture rates.

Recently, a method was described in which the change in capacitance of

a PN-junction was used to determine capture rates^{65,66)}. A PN-junction is reverse biased, the investigated impurity is emptied by carriers through the illumination of light and the capacitance is measured. During a short time interval, Δt , the reverse voltage is brought to zero and after that the capacitance is again measured. The change in capacitance is now a measure of the number of levels filled during time Δt and by repeating the measurement for different values of Δt , the carrier lifetime is obtained. This method has been used for a number of impurities in GaP, GaAs^{66,67)} and Si⁶⁸⁾.

Examples of other methods are measurements of the photoelectromagnetic effect⁶⁹⁾, the time dependence of space charge limited currents⁷⁰⁾, double pulse measurements on P⁺I⁻N-structures⁷¹⁾ and the use of an alternating current distortion technique on PN-junctions⁷²⁾.

Measurement techniques developed up to 1958 are reviewed in ref 59. A modern survey on this subject seems to be lacking in the literature.

III.2 Emission rates

It has become possible in recent years to measure thermal and optical emission rates for a large number of systems due to the development of new measurement techniques using PN-junctions. A number of transient measurement methods have been developed by Sah et al⁷³⁾ and a steady state method has been developed by Björklund and Grimmeiss⁷⁴⁾.

In the transient methods, time constants and the boundary values of currents and capacitances are the parameters reflecting the emission

properties of the deep centers. When measuring current transients in PN-junctions, the interpretation of the results is complicated by the fact that the charge measured in the outer circuit is not equal to the charge created in the space charge region. The reason for this is that a displacement current is present during the excitation process. These problems have been solved in paper III where the influence of displacement currents on deep impurity induced transients has been investigated.

In the steady state method, two light sources with different intensities are used and the emission properties are obtained through a small signal measurement. Thermal and optical activation energies are given by measurements of thermal emission rates versus temperature and optical emission rates versus photon energy. Both methods have been used in the following papers and the reader is referred to these articles for details and further references.

A variation of the steady state method was used in ref 75, where the absorption of light in neutral material was the parameter measured. Other methods are a recently developed photoconductivity method ⁷⁶⁾ and the measurement of excitation spectra in luminescent materials ⁷⁷⁾.

IV. GOLD DOPED SILICON

IV.1 Electronic properties

Gold as an impurity in silicon has become of great technical importance for controlling lifetimes. The first investigations, made in the fifties ^{78,79)}, were followed by a large number of measurements, which have

made Si:Au one of the most extensively investigated deep impurity systems. Gold introduces two energy levels in silicon, one acceptor level about 0.61 eV from the conduction band and one donor level about 0.35 eV from the valence band. A thorough investigation of the optical activation energies has been made by Braun and Grimmeiss⁸¹⁾. They found that the spectral distributions of photoionization cross sections could be fitted by a simple theory due to Lucovsky⁵²⁾, thus indicating that the impurity potential is very narrow. These results were compared to a refined theory in ref 53 taking the rather complicated structure of the valence band in silicon into account.

The gold impurity is capable of capturing two electrons: when empty it contains one positive electron charge, when filled by one electron it is neutral and when filled by two electrons it contains one negative charge. The two levels always appears at the same concentrations and they obviously belong to the same gold atom. This means that gold acts as both a donor and an acceptor and that the two levels (fig 4) are

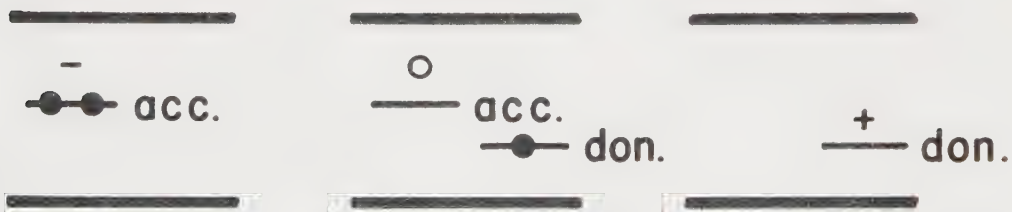


Fig. 4

coupled in the sense that when the impurity is filled by two electrons, the first excited electron is always taken from the acceptor level and the second excited electron from the donor. Conversely, a hole in the

donor level must be excited to the valence band before a hole in the acceptor. From this, it follows that, due to the very high recombination rate of majority carriers compared to that of minority carriers, in a neutral n-type material only the acceptor level can be observed and in a p-type material only the donor level⁸⁰⁾.

Gold increases the resistivity for n-type materials as well as for p-type. Some problems in the resistivity dependence of the gold concentration still remain unsolved³⁾⁸⁰⁾. It has been proposed that another gold state might appear, located 0.033 eV above the valence band and being an electrically active complex of gold with other defects⁸³⁾. The discrepancy for resistivity between theory and experiment can be eliminated³⁾ by assuming that the concentration N_{CC} of the complex center increases approximately as $N_{CC} = 4.5 \cdot 10^{-36} N_{Au}^3 \cdot \text{cm}^{-3}$.

Capture cross sections for the gold acceptor state have been determined in paper II. Results obtained by other authors are also tabulated there, but, after the publication of paper II, more results have become available in the literature and a complete list is shown in table 1. Because the capture cross sections are temperature dependent comparison must be made between results given at the same temperature. All cross sections in table 1 are given at 77 K except in one of the columns. The capture cross sections for electrons to the acceptor is only weakly dependent on temperature^{62,68,112)} and the values in this column are therefore given at different temperatures. As can be seen, the values differ considerably among different authors. As pointed out in paper II, one possible source of error comes from the determination of gold concentration.

TABLE 1

Author	Acceptor state		Donor state		Ref
	(77-300 K) s_n^t	(77 K) s_p^t	(77 K) s_n^t	(77 K) s_p^t	
Bemski 1958	$5 \cdot 10^{-16}$	$1 \cdot 10^{-15}$	$1 \cdot 10^{-13}$	10^{-16}	62
Davis 1959	$3 \cdot 10^{-15}$		$6 \cdot 10^{-14}$		84
Fairfield 1965	$1.7 \cdot 10^{-16}$	$1 \cdot 10^{-14}$		$2.4 \cdot 10^{-15}$	85
Zohta 1972	$5 \cdot 10^{-15}$				86
Pals 1974	$1.3 \cdot 10^{-16}$				68
Kassing 1974	$8 \cdot 10^{-16}$				87
Paper II	$2 \cdot 10^{-15}$	$1 \cdot 10^{-14}$			88
Braun 1975			$6 \cdot 10^{-14}$		89

Photo-ionization cross sections have been measured in ref 81 and 82 and thermal emission rates were investigated in ref 82 and paper II.

IV.2 Space charge effects in high ohmic Si:Au

Since the appearance of theories for the single and double injection of carriers into insulators^{90,91)}, a large number of deep level systems has been investigated for space charge effects. Gold doped double injection devices of silicon were investigated by Moore et al⁹²⁾. The material exhibited current controlled negative differential resistance and current oscillations in the pre-breakdown region. The frequency of these oscillations were proportional to the concentration of gold and could be varied in the region 10-100 MHz when the gold concentration was varied between 4 and $40 \cdot 10^{15} \text{ cm}^{-3}$. A theory for oscillations in

systems of this kind has been given by Weber and Ford ⁹³⁾. Double injection oscillations in the 100 KHz range and oscillations which seem to be due to single injection are reported in ref 94 and 95.

IV.3 Atomic properties

One reason why gold has become technically so important as a dopant in silicon is its large capture cross sections; it belongs to the "giant trap"-group mentioned in section II.4. Other reasons are its chemical resistance, large diffusion coefficient and high solubility ³⁾ compared to other deep impurities. When diffusing gold into silicon slices, U-shaped concentration profiles are found with very high gold concentrations at the surfaces ⁹⁷⁾. Using a temperature of 1000 °C and a diffusion time of 40 minutes, a gold concentration of about $5 \cdot 10^{15} \text{ cm}^{-3}$ is reached in the central part of a 0.5 mm thick silicon disk. This concentration has been found to be dependent on the density of the dislocation in the starting material. This supports a model for the diffusion mechanism in which the fast interstitial diffusion of gold is accompanied by the transition of interstitial atoms into substitutional sites by the annihilation of lattice vacancies ^{97,98)}.

IV.4 Summary of known Si:Au properties

Because of the large number of investigations on Si:Au, it might be interesting to get an overall view of how much is known about the Au-center in silicon experimentally and theoretically. An attempt to do this has been made in table II. In the table, "I" means that satisfactory experimental results or thorough theoretical

explanations have been reached, "0" that no information is available and "1/2" indicates qualitative information. The information obtained from such a table is of course very approximate: a detailed view can only be obtained by going to the references of the right column.

TABLE 2

Quantity	Exp	Theory	Ref
Act energy ΔE	1	0	79, 81, 82, paper II
Type of level	1	0	80
e_n^0, e_p^0	1	1	81, 53
c_n^0, c_p^0	0	1	82
e_n^t, e_p^t	1	0	81, paper II
c_n^t, c_p^t	1	1/2	see table 1, 33, 35
Temp dep of ΔE	1	0	paper I (acceptor only)
Surrounding lattice	1/2	0	81
Degeneration	1/2	0	paper II (acceptor only)
Details of impurity potential and wave function	0	0	
Diffusion properties	1	1/2	97, 98

V. SULFUR DOPED SILICON

V.1 Electronic properties

Sulfur belongs to group VI in the periodic table and it is therefore natural that it exhibits donor behaviour in the group IV element silicon. Four donor levels have been found (see paper IV) at about 0.1, 0.18, 0.37 and 0.61 eV respectively from the conduction band. It has been suggested⁹⁹⁾ that the 0.1 and 0.37 eV-levels belong to a double donor coming from a pair of sulfur atoms, while the 0.18 and 0.61 eV-levels belong to another double donor coming from an isolated sulfur atom. The double donor nature implies that the center carries two positive electron charges when empty, one positive charge when filled by one electron and that it is neutral when filled by two electrons. As mentioned in section II.2, sulfur is a very interesting impurity in silicon because the two elements are isocoric, making it possible to describe sulfur by KL-EMT⁷⁾. Excited states are therefore expected to appear and have been found in ref 100 - 104 and in paper IV.

The only available measurement of capture rates in the literature can be found in ref 105 which also contain results on thermal emission rates. The measurement of capture rates is however made in the space charge region of a PN-junction and, due to its very high field dependence, no good estimate can be made for the capture rate in neutral material.

Photoionization cross sections for electrons from the deepest sulfur level were measured in ref 104 and in paper IV the photoionization cross sections for the four transitions associated with the 0.37 and 0.61 eV-levels have been measured. The optical activation energies from the valence band to the level and from the level to the conduction band are also given in

paper IV.

V.2 Space charge effects in high ohmic Si:S

Investigations of sulfur doped high ohmic injection devices have been made by Lebedev and co-workers^{107,108)}. In the case of n-type silicon, double injection samples exhibited current-controlled negative differential resistance (S-type) and for p-type single injection samples voltage-controlled (N-type) characteristics were found. This is an expected consequence of the double donor behaviour of sulfur. When the current in the pre-breakdown region is carried by electrons, a normal double injection effect might be expected: when carried only by holes, however, the capture mechanism proposed by Ridley and Watkins¹⁰⁶⁾ would give an N-type IV-characteristic due to repulsive sulfur centers.

V.3 Atomic properties

Sulfur in silicon has much a lower diffusion coefficient and solubility than is the case for gold^{3,96)}. To reach a concentration of about $5 \cdot 10^{-15} \text{ cm}^{-3}$, a diffusion temperature of around 1200 °C during about 20 h is required. Another problem which arise in the doping procedure is that sulfur reacts with the silicon producing SiS and SiS₂. This causes mass transport of silicon and erosion of the samples. This can, however, be avoided by using the technique described in paper IV.

The position of sulfur centers in the silicon lattice has been established by Ludwig¹⁰⁹⁾ by paramagnetic resonance studies. This investigation shows that sulfur goes into silicon both as atomic sulfur and as

a complex S_2 .

The atomic sulfur corresponds to the deepest energy level at 0.61 eV and was found to have tetrahedral symmetry. It was not, however, possible to conclude whether this center occupies a substitutional or an interstitial site with a similar arrangement of neighbours. The splitting factor was found to be close to 2 indicating that the ground state is orbitally non-degenerate.

The S_2 -complex was found to be associated with the 0.37 eV-level being built up by a near pair of two substitutional sulfurs or two sulfurs in equivalent interstitial sites.

V.4 Summary of known Si:s - properties

A similar rough overall view for Si:S as in section IV.4 for gold is given in table 3.

VI. CONTRIBUTIONS BY THIS THESIS

VI.1 Gold doped silicon, paper I and II

In spite of gold doped silicon being one of the most technically important deep impurity systems, the recombination mechanism connected with this center is not entirely understood. From optical measurements⁸²⁾, values of the radiative capture cross sections of about 10^{-21} cm^2 have been obtained, while the thermal measurements in paper II give cross sections in the region $10^{-14} - 10^{-15} \text{ cm}^2$. It therefore seems obvious that thermal activation of the center is not a photon process and it would

TABLE 3

Quantity	Exp	Theory	Ref
Act energy ΔE	1	1	101, paper IV, 7
Type of level	1	1	110, 105
e_n^o, e_p^o	1	1	104, paper IV
c_n^o, c_p^o	0	0	
e_n^t, e_p^t	1	0	105
c_n^t, c_p^t	1/2	0	105
Temp dep of ΔE	1	1	99, paper IV
Surrounding lattice	1	1	109, 7
Degeneration	1	1	109
Details of impurity potential and wave function	0	0	
Diffusion properties	0	0	

be interesting to compare optical threshold energies ⁸¹⁾ with thermal activation energies. This was carried out for the gold acceptor in paper II. In determining thermal activation energies, it is important to take into account the temperature dependence of capture cross sections and of the energy level itself. In earlier measurements, this has either been completely neglected or the estimates of the temperature dependences of these parameters used have been wrong. By making independent measurements of the temperature dependence of the acceptor energy position (paper I) and of the capture rate for holes, the

thermal activation energies were found at the same values as the optical threshold energies to within a few meV. This has for the first time brought thermal emission data, capture data and optical data into agreement. Similar results have later been published in ref 111 and 112.

VI.2 Interpretation of deep impurity induced transients in PN-junctions, paper III

When making deep impurity induced transient measurements on PN-junctions, not all of the charge created inside the space charge region will be measured in an external circuit due to the influence of displacement currents. The ratio between the measured and created currents inside the space charge region can be written as a factor D . This factor, which obviously influences the interpretation of transient data, has earlier in some cases been taken to be $D = 1$ and in other cases to be $D = 2$. In paper III, it is shown that the D -factor can take any value between 1 and infinity depending on the experimental situation. A method for the experimental determination of the D -factor is also given.

VI.3 Sulfur doped silicon, paper IV

All optical threshold energies and the spectral distributions of photo-ionization cross-sections for two sulfur impurities are measured for the first time in paper IV. The spectral distribution curves are fitted to theoretically calculated curves and it is found that the impurity potential for holes are different from that for electrons. The sum of binding energies for holes and electrons is found to exceed the band gap value of silicon, which is in accordance with an assumed double donor behaviour

of the two centers. All distributions exhibit a more or less pronounced structure. The temperature dependence of this structure together with the temperature dependence of the threshold energy is used for the deepest lying impurity level to determine the variation in energy positions for different temperatures. It is found that the deepest lying sulfur impurity is pinned to the conduction band in accordance with the KL-EMT approach. The structure of the spectral distribution curves is believed to arise from excited states and from phonon interaction.

VII. CONCLUSIONS

In this introductory article, a review of theoretical and experimental progress in studies of deep impurities has been given with its interest being focused primarily on gold and sulfur in silicon. The intention has been to give an outline of the environment, in which the results in this thesis must be placed. Some properties of deep impurities have been described in more detail than others and many properties have not been mentioned at all. The selection has, however, not been determined by a judgement of "importance", but more by what might be needed by the non-specialist when reading the following papers.

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Temperature dependence of the gold acceptor energy level in silicon

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Abstract

Using the spectral distribution of the optical emission rates it is shown that the gold acceptor energy level in silicon is probably pinned to the conduction band in the temperature range between 90 K and 242 K.

Temperature dependence of the gold acceptor energy level in silicon

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Gold as an impurity in silicon is widely used for controlling charge carrier lifetimes, and its properties have been studied extensively. In recent years the optical¹⁾²⁾ and thermal¹⁾³⁾ emission rates for the gold acceptor state have been investigated using new measurement techniques⁴⁾⁵⁾. However, in most cases capture cross sections calculated from thermal emission rates by using the equations of detailed balance differ considerably from published data. Furthermore, there is also considerable disagreement in the published values for the energy position of the gold acceptor level deduced from the temperature dependence of the thermal emission rates. In a recent letter⁶⁾, Parillo and Johnson presented a new interpretation aimed at resolving this anomaly and to bring available data into consonance. They take into account the temperature dependence of $E_C - E_T$ and $E_T - E_V$, where E_C is the bottom of the conduction band, E_V the top of the valence band and E_T the effective energy level of the gold acceptor impurity centre, which includes the excited states and their degeneracy. The authors assumed without proof that the gold acceptor state remains in the same relative position with respect to the two band edges as the band gap changes with temperature. This assumption is in disagreement with experimental results published by Sah et al⁷⁾, who found that the energy distance between the gold

acceptor level and the conduction band changes linearly with temperature, giving a value for the temperature coefficient of $-4.5 \cdot 10^{-4}$ eV/K. In this letter, we will present experimental results which appear to indicate that in contrast to the assumption of Parillo and Johnson and the experimental data of Sah et al the gold acceptor level is pinned to the conduction band for temperatures below 242 K.

Using the measurement technique described in ref 2, the energy position of the gold acceptor impurity centre has been determined from the spectral distribution of the optical emission rates for electrons, e_{ns}^0 , and for holes, e_{ps}^0 , respectively. It has earlier been shown²⁾ that the extrinsic photocurrent density J_R^0 of a reverse-biased P-N junction with a single impurity level illuminated with photons of energy $h\nu_s$ and intensity I_s at low temperatures is given by

$$J_R^0 = B \cdot b \cdot e_{ns}^0 \quad (1)$$

where

$$b = \frac{e_{ps}^0}{e_{ns}^0 + e_{ps}^0} \quad (2)$$

is the steady-state electron occupancy factor of the gold acceptor level and B is a constant involving an effective space charge region⁸⁾ and the total gold concentration. If the P-N junction is illuminated with light of high intensity I_s and constant photon energy $h\nu_s$ (to establish a constant b), it can be shown (cf. ref. 2 eq 15) that the increase in the photocurrent ΔJ_R^0 due to the illumination from a second light source with low intensity

I_p and varying photon energy $h\nu_p < E_c - E_{Au} +$ can be written as

$$\Delta J_R^0 = B (b^2 e_n^0 + (1-b)^2 e_p^0). \quad (3)$$

Hence, the small signal photocurrent ΔJ_R^0 is proportional to e_n^0 or e_p^0 depending on whether $b = 1$ or 0 . Because the optical emission rates are linearly dependent on the light intensity, the spectral distribution of e_n^0 and e_p^0 obtained for constant intensity I_p are proportional to the spectral distribution of the photoionization cross sections σ_n^0 and σ_p^0 at photon energies $h\nu_p$.

For the determination of $E_T - E_V$, we used a photon energy $h\nu_s = 0.57$ eV for the pumping light. For this energy, $e_{ps}^0 = 0$ ¹⁾²⁾ and hence $b=0$. The small signal photocurrent ΔJ_R^0 is then given²⁾ (cf. eq 3) by $B e_p^0 = \text{const. } e_p^0$ for all photon energies smaller than about 0.8 eV. At higher temperatures, for which the thermal excitation processes no longer can be neglected, the steady state electron occupancy factor is

$$b = \frac{e_{ps}^0 + e_p^t}{e_{ps}^0 + e_p^t + e_{ns}^0 + e_n^t} \quad (4)$$

where e_n^t and e_p^t are the thermal emission rates of electrons and holes respectively for the gold acceptor state. However, because for temperatures below 300 K $e_n^t / e_p^t > 10^1$ ¹⁾, b^2 will never exceed a value of 0.01. Thus, taking into account a small value of b at higher temperatures which is independent of $h\nu_p$, the spectral distribution of e_p^0 was measured for six distinct temperatures using eq 3 (fig 1). To demonstrate that the

curve form is the same for all six temperatures, the curves have been normalized to the 90K-data. This has been achieved by shifting the curves to higher energies by 4 meV at 104K, 10 meV at 152K, 14 meV at 202K, 22 meV at 225K and 28 meV at 242K, thus showing that $E_T - E_V$ is temperature dependent. A comparison of the temperature dependence of $E_T - E_V$ with that for the energy band gap⁹⁾ (fig 2) indicates that in both cases a similar temperature dependence exists. For the determination of $E_C - E_T$, the steady state electron occupancy factor should be as large as possible. We used a photon energy $h\nu_s = 0.85$ eV for the pumping light giving $b \approx 0.8$ ²⁾. At photon energies $h\nu_p$ smaller than about 0.7 eV, for which $e_p^0 < e_n^0$, it follows from eq 3 that ΔJ_R^0 is mainly determined by e_n^0 . In the region above 0.7 eV, however, e_p^0 becomes larger than e_n^0 and hence will contribute to ΔJ_R^0 . In fig.3, the spectral distribution of ΔJ_R^0 for $b \approx 0.8$ is shown for three different temperatures. No shift in energy and thus no temperature dependence of $E_C - E_T$ is observed although the energy bandgap of silicon varies about 14 meV in this region. It can further be seen that the influence of e_p^0 is so small that the curves are not affected by the temperature dependence of e_p^0 . Reliable measurements could only be performed for temperatures below 200K because at higher temperatures b decreases strongly due to thermal emission processes¹⁾.

The temperature dependences of $E_T - E_V$ and $E_C - E_T$ thus indicate that the gold acceptor state in silicon might be pinned to the conduction band when the temperature is varied between 90K and 242K. This result should be considered when the energy position of the gold acceptor level is calculated from the temperature dependence of thermal emission rates.

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Figure captions

- Fig 1 Normalized spectral distribution of σ_p^0 . The energy scale for the 104K, 152K, 202K, 225K and 242K-values are shifted to higher energies by 4, 10, 14, 22 and 28 meV respectively.
- Fig 2 Comparison between the temperature dependence of $E_T - E_V$ with that for the energy band gap for silicon taken from the data of Bludau et al⁹⁾ (solid curve).
- Fig 3 Spectral distribution of ΔJ_R^0 at $b \cong 0.8$. ΔJ_R^0 is proportional to e_n^0 at energies below about 0.7 eV.

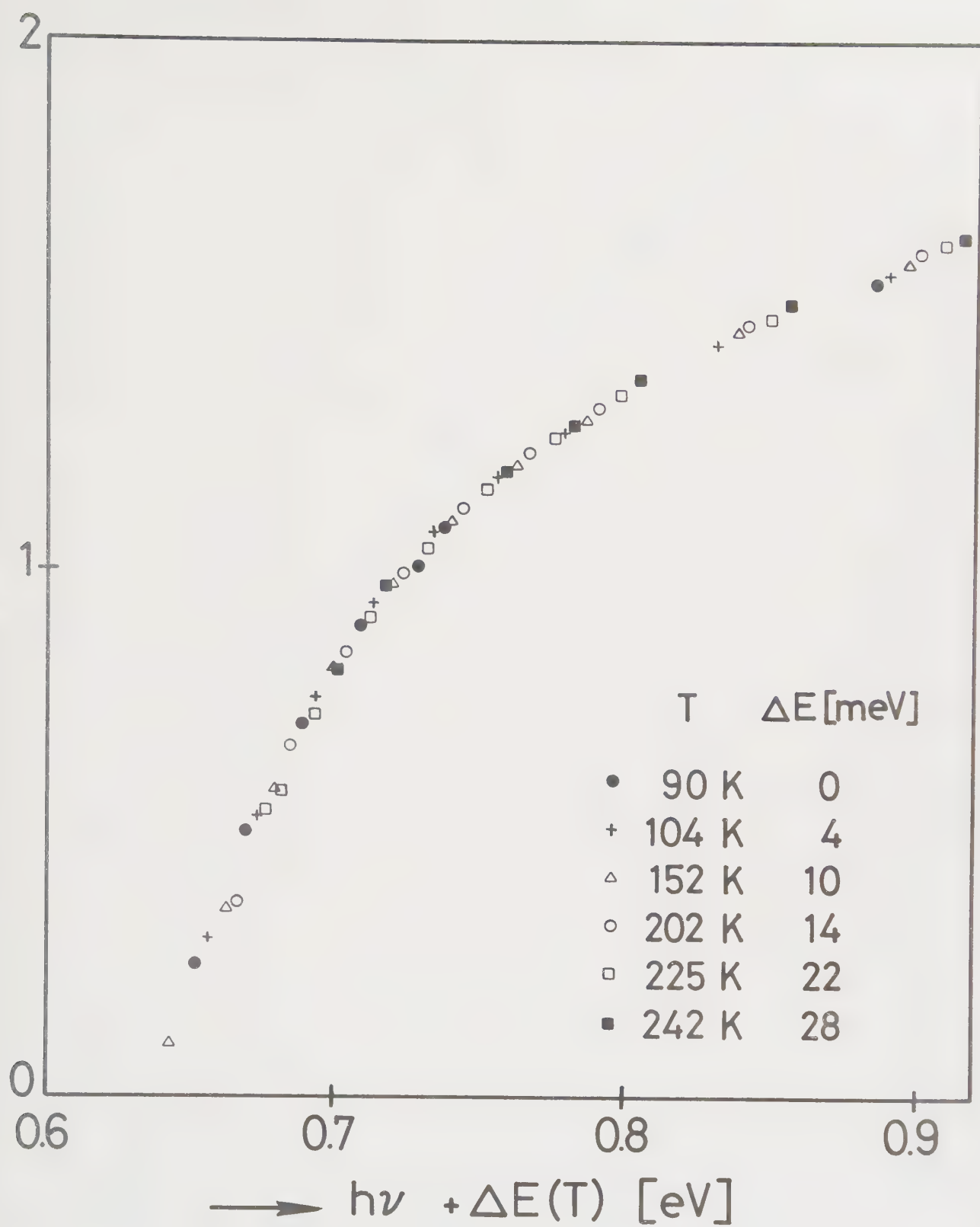


Fig. 1

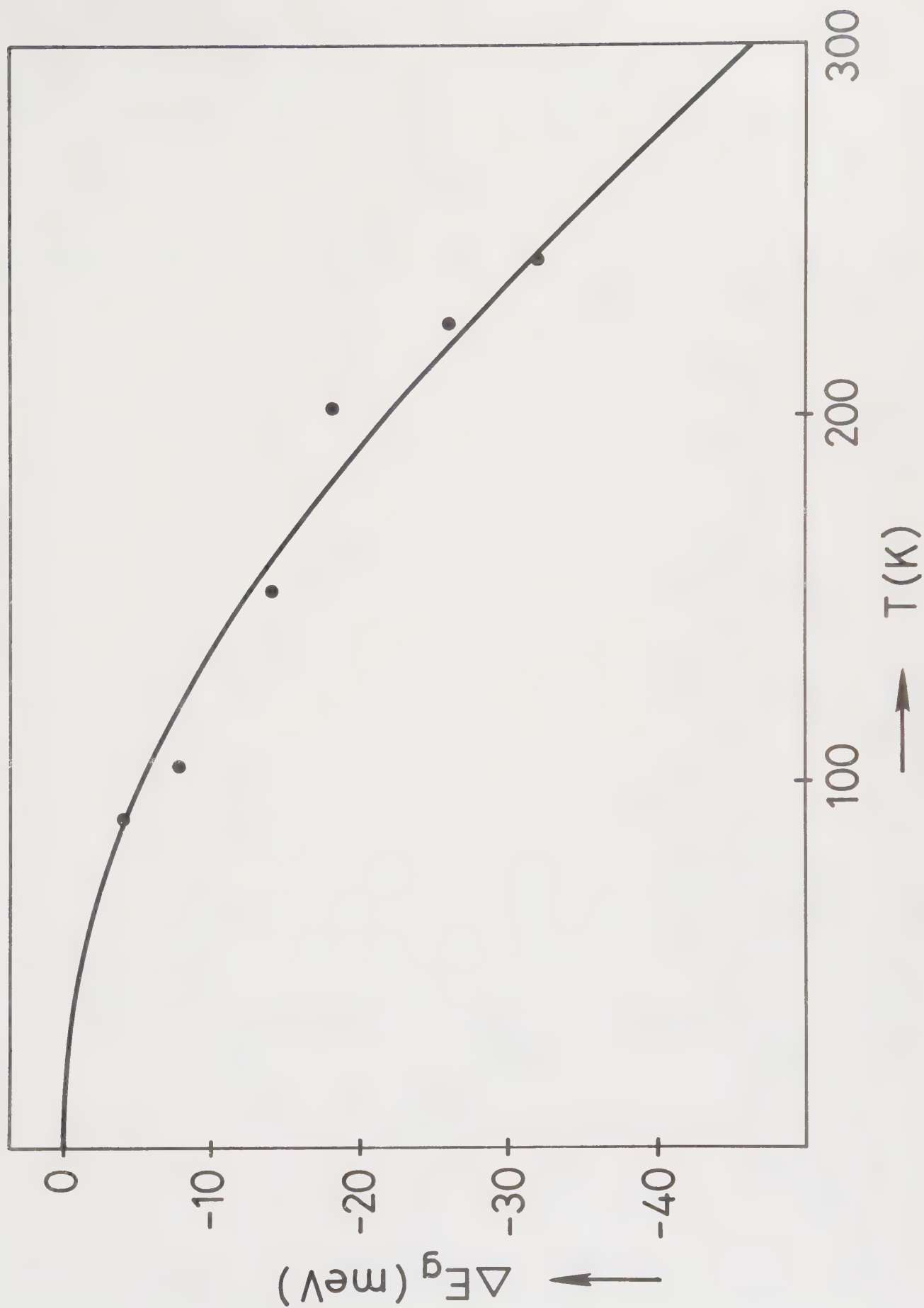


Fig. 2

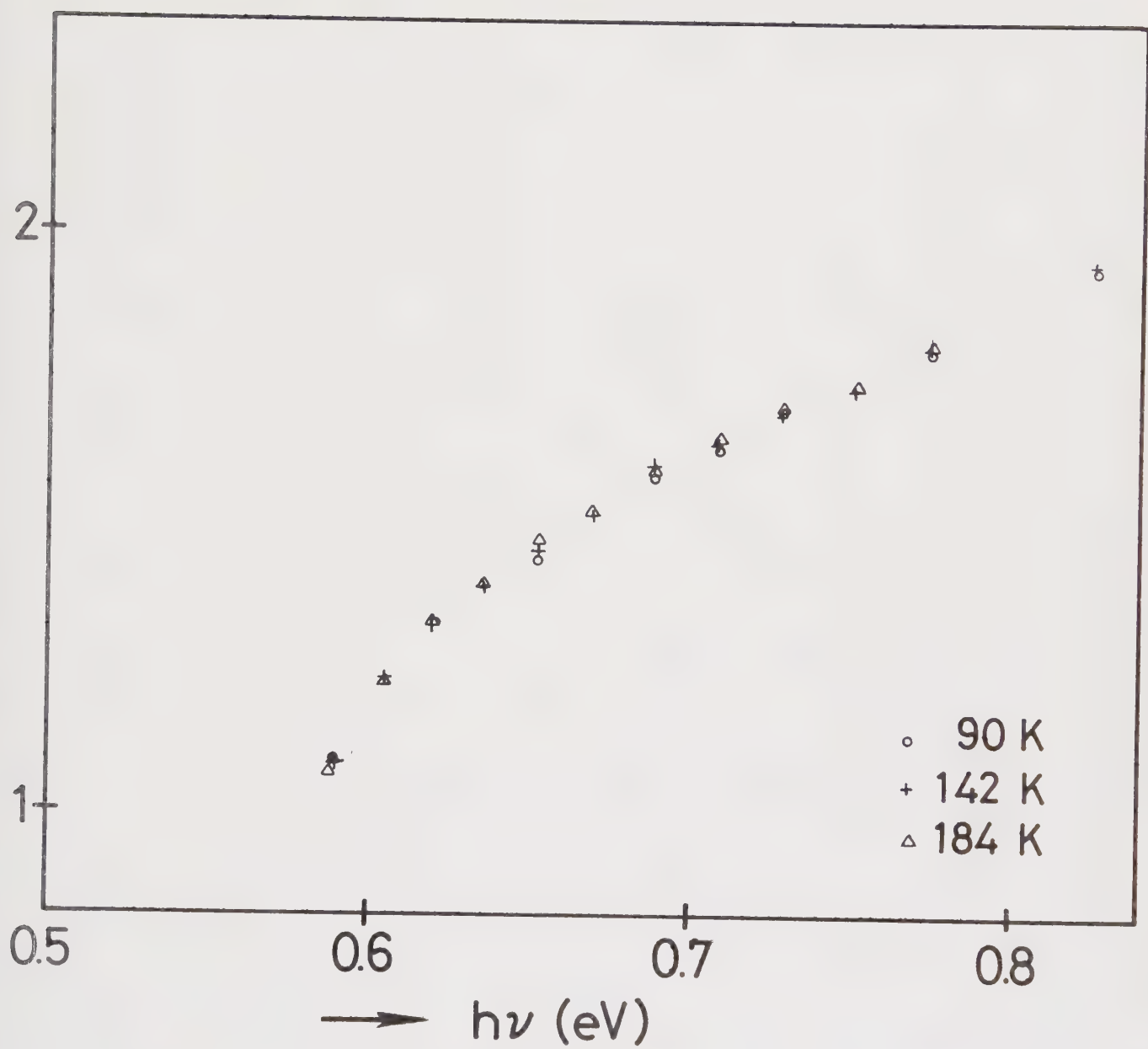


Fig. 3

Thermal activation energy of the gold acceptor level in silicon

by

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Abstract

The thermal emission rates of electrons and holes at gold-acceptor levels in silicon have been measured in P+N junctions as a function of temperature using the dark current transient method. From these measurements, the linearly-extrapolated absolute zero thermal activation energies of electrons (553 meV) and holes (641 meV) have been determined taking the temperature dependence of the hole capture rate into account. The latter has been determined by measuring the diffusion length at different temperatures. Using earlier optical results which showed that the energy-distance of the gold-acceptor centre from the conduction band is independent of temperature the thermal activation energies of electrons and holes are calculated as a function of temperature. These results are to within a few meV in agreement with previously-published optical data. Using the principle of detailed balance in thermal equilibrium, values of $c_p^t = 1 \cdot 10^{-7} \text{ cm}^3/\text{s}$, $c_n^t = 2 \cdot 10^{-8} \text{ cm}^3/\text{s}$ and $g_A \approx 3.2$ are estimated for the capture rates and the degeneracy factor respectively at room temperature.

Thermal activation energy of the gold acceptor level in silicon

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I. Introduction

Gold causes in silicon deep impurity centres, one acceptor level lying at about 0.55 eV below the conduction band edge and one donor level at about 0.35 eV above the valence band edge. Although the physical properties of these impurity levels have been studied extensively¹⁻⁸⁾, there exists still considerable disagreement in the published values for the energy position of the gold acceptor level as deduced from thermal activation energies. A summary of the reported values is given in table I. These values have been obtained from the slopes of the logarithm of the resistivity ρ , the Hall coefficient R_H or the thermal emission rates e^t vs T^{-1} after corrections for the temperature dependence of the density of states, the thermal velocities or mobility. Because no higher-order temperature-dependence for the top of the valence band E_V , for the bottom of the conduction band E_C and for the energy level E_T have been assumed, these ionization energies correspond to the linearly-extrapolated absolute zero-energy values and not to the energy value at the measuring temperature. The sum of the two thermal ionization energies can therefore be expected to be equal to the linearly extrapolated band-gap energy E_{g0} ⁷⁾ at $T = 0$ K (fig. 1). The temperature dependence of the energy band gap is, however, not linear for temperatures below 300K. Thus, the value of E_{g0} depends on the temperature region

in which the measurements are performed. The value of E'_{go} in Si is about 1.195 eV in the region 200-300 K⁹⁾, while, for higher temperatures, $E_{go} \geq 1.21$ eV (fig. 1). It is readily seen from table I that in some cases the published data deviate considerably from these E_{go} -values.

Deep level impurities are regarded as having rather narrow potentials. Electrons and holes are therefore more strongly bound into more localized orbits than for hydrogen-like "effective-mass-donors" and "-acceptors". Together with the lattice misfit, one might therefore expect lattice relaxations. This would imply that the sum of the threshold energies $(E_C - E_T) + (E_T - E_V)$, obtained from optical absorption measurements, exceed the value of the band gap energy E_g . However, for gold acceptors in silicon, it has recently been shown¹⁰⁾ that the optical activation energies for electrons and holes sum up very accurately to the band gap value. The purpose of this paper is therefore to reinvestigate the thermal activation energies of the gold acceptor level in silicon and to compare these results with optical measurements.

Using P+N - junctions, thermal ionization energies have been obtained from dark current transient techniques¹¹⁾ taking the temperature dependence of the capture cross sections into account.

Furthermore, by combining these transient measurements with steady state measurements of the dark reverse current, the sum of the two ionization energies is determined very accurately if recombination processes at the ends of the transition region of the PN-junction are considered. It will be shown that in both cases

the ionization energies add up to the extrapolated zero band gap value E_{go} to within a few meV.

Finally, by using recent results¹²⁾ which indicate that the gold acceptor level is pinned to the conduction band, the temperature dependence of the thermal ionization energies is discussed and the obtained results are compared with the optical activation energies quoted previously.

II. Theoretical background

The experiments described in this paper make use of dark current transients obtained from thermal excitation processes in the transition regions of reverse biased PN-junctions doped with gold impurities. From these measurements, the thermal emission rates of electrons and holes e_n^t and e_p^t are directly obtained¹¹⁾. At thermal equilibrium, the thermal emission rates of electrons and holes from the gold acceptor level in silicon can be expressed as

$$e_n^t = g_A c_n^t N_C \exp \left(\frac{E_T - E_C}{kT} \right) \quad (1)$$

$$e_p^t = g_A^{-1} c_p^t N_V \exp \left(\frac{E_V - E_T}{kT} \right) \quad (2)$$

Here, $c_n^t = \sigma_n^t \cdot \theta_p$ are the thermal capture rates of electrons and holes at the gold acceptor level, σ_n^t and σ_p^t are their thermal capture cross sections and θ_n and θ_p are their thermal (average) velocities. g_A is a (temperature-independent) degeneracy-factor,

N_C and N_V are the effective density of states in the conduction and valence band and E_T is the energy level of the gold acceptor impurity centre. Recalling that N_C and N_V are proportional to $T^{3/2}$ and that θ_n and θ_p increase with the square root of the temperature, eq(1) and (2) can be written as

$$e_n^t = A_n \cdot T^{2-N} \exp \left(- \frac{\Delta E_{no}}{kT} \right) \quad (3)$$

$$e_p^t = A_p \cdot T^{2-P} \exp \left(- \frac{\Delta E_{po}}{kT} \right) \quad (4)$$

where A_n and A_p are constants containing all temperature-independent factors and ΔE_{no} and ΔE_{po} are the linearly-extrapolated thermal ionization-energies at $T = 0$ K. N and P are given by the temperature-dependence of the thermal capture cross sections $\sigma_n^t \sim T^{-N}$ and $\sigma_p^t \sim T^{-P}$. Thus, from the slopes of the values of $\log (e_n^t/T^{2-N})$ and of $\log (e_p^t/T^{2-P})$ vs $1/T$ the linearly-extrapolated absolute zero energy of the acceptor level relative to E_C and E_V can be determined if N and P are known.

III. Temperature dependence of the thermal capture cross sections

For most impurities in germanium and silicon, it is found empirically¹³⁾ that the thermal capture cross section for a neutral centre is either independent of or else only weakly dependent on temperature, while for attractive centres the cross section is proportional to T^{-K} . A review of the theoretical aspect is given in ref. 14.

Defining the lifetime of holes in the neutral N-region by

$$\tau_p = (\sigma_p^t \theta_p N_{TT})^{-1}, \text{ where } N_{TT} \text{ is the concentration of gold acceptor}$$

levels, and using the Einstein relation together with the expression for the hole diffusion length $L_p^2 = D_p \tau_p$, the thermal capture cross section of holes can be expressed as:

$$\sigma_p^t = \frac{kT \mu_p}{q \theta_p N_{TT} L_p^2} \quad (5)$$

The mobility μ_p in eq (5) is the drift mobility of holes and is described by

$$\frac{1}{\mu_p} = \frac{1}{\mu_L} + \frac{1}{\mu_I} \quad (6)$$

where μ_L is the component of the mobility which is determined by lattice scattering and μ_I the component which arise from impurity scattering. Hole mobilities have recently been measured in silicon by Canali et al¹⁵⁾. From their results the lattice mobility in the temperature range 100-200K is approximately ascribed by the expression $1.1 \cdot 10^7 \cdot T^{-1.7}$. To investigate the influence of the density of scattering centers on the mobility, the Conwell-Weisskopf formula¹⁶⁾ has been successfully used¹⁷⁾⁻¹⁹⁾ for the mobility component arising from impurity scattering. Following the intentions of ref. 17, we have calculated the total mobility μ_p versus temperature from eq (6) by taking μ_L from ref. 15 (fig. 2). The average slope of $\log \mu_p = f(\log T)$ is -1.5 in the temperature range 150-250K.

The hole diffusion length L_p has been measured by illuminating the N-region of a reverse-biased P+N-junction with strongly absorbed

monochromatic light²⁰⁾. The hole concentration $p(x)$ as a function of the distance from the illuminated surface is then given by

$$p(x) = p(0) \cdot \exp\left(-\frac{x}{L_p}\right) \quad (7)$$

with the positive x -axis into the semiconductor. Denoting the distance of the transition region from the illuminated surface by x_n , the photocurrent J_R^O observed is then given by

$$J_R^O = B \cdot \exp\left(-\frac{x_n}{L_p}\right) = B' \cdot \exp\left(-\frac{W}{L_p}\right) \quad (8)$$

where B and B' are constants and W is the width of the transition region. Thus plotting the logarithm of the photocurrent against W at different temperatures, which can be calculated from the dark capacitance, the hole diffusion length is readily obtained from the slope of the straight lines (fig. 3). These measurements indicate that L_p^2 increases almost linearly with temperature (fig. 4). Hence, approximating the temperature dependence of the hole mobility μ_p by $T^{-1.5 \pm 0.1}$ (fig. 2), eq (5) can be rewritten as

$$\sigma_p^t = C \cdot T^{-2.0 \pm 0.1} \quad (9)$$

where C is again a constant. This result deviates substantially from results obtained by Bemski²¹⁾ who found, from transient measurements, a value of $P=4$ for the gold acceptor in silicon. However, by considering the literature on capture cross-sections

for different dopants in Ge and Si¹³⁾, such a temperature dependence as T^{-4} is found to be anomalously high. Inserting a value of 2.0 for P in eq (4), the thermal emission rate for holes from the gold acceptor level in silicon can now be expressed as

$$e_p^t = A_p \cdot \exp \left(- \frac{\Delta E_{po}}{kT} \right) \quad (10)$$

Similarly, we obtain from eq (3) for $N = 0$

$$e_p^t = A_n \cdot T^2 \exp \left(- \frac{\Delta E_{no}}{kT} \right) \quad (11)$$

IV. Experimental details

All measurements were performed on P+N junctions with an area of about 1mm^2 , where N is a lightly-doped epitaxial layer with about $6 \cdot 10^{15} \text{cm}^{-3}$ shallow donors grown on the P+ substrate with about $5 \cdot 10^{18} \text{cm}^{-3}$ shallow acceptors (fig. 5). The samples were gold-diffused at 890°C giving a homogeneous gold impurity concentration N_{TT} of about $3 \cdot 10^{14} \text{cm}^{-3}$. Those junctions which were used for the investigation of the hole diffusion-length were in addition covered with an aluminum guard ring to make sure that optical excitation occurred only in the neutral N-region. The diffusion length measurements were even performed with samples containing a gold concentration of $3 \cdot 10^{15} \text{cm}^{-3}$. In all cases, the diffusion length is determined by the presence of the gold acceptor levels.

As light source, a xenon lamp with a Bausch & Lomb high-intensity grating monochromator was employed. An interference filter

(4500 Å) and a glass-filter (BG18) were used to suppress stray light and higher orders of diffracted light. Current transients with time constants greater than about 10^{-2} s were measured with a Nicolette 1090 digital oscilloscope and a Keithley 427 current amplifier. For shorter transient times, a Tektronix 549 oscilloscope was used.

V. Thermal emission rates

Thermal emission rates were obtained from the dark-current transient wave forms¹¹⁾ (fig. 6). The technique involved the measurements of the decay time constant τ and the initial and final dark current $I_R^t(0)$ and $I_R^t(\infty)$, respectively, when the junction voltage is switched from zero to a large reverse bias $-V_R$. It has been shown that the thermal emission rates e_n^t and e_p^t can be calculated from the transient waveforms according to the following relations:

$$\frac{e_n^t}{e_p^t} = D \cdot \frac{I_R^t(0)}{I_R^t(\infty)} - 1 \quad (12)$$

$$e_n^t + e_p^t = \tau^{-1} \quad (13)$$

It should be noted that the factor D in eq (12) depends on the doping profile and is equal to 2 only if the junction has a low degree of compensation and is perfectly abrupt.

VI. Thermal ionization energies

If it is assumed that the detailed balance condition expressed by equations (1) and (2) remains valid in the space-charge region

of the P+N-junction, the linearly-extrapolated thermal ionization energies for $T = 0$ K are readily obtained according to equations (10) and (11) by plotting $\log (e_n^t \cdot T^{-2})$ and $\log (e_p^t)$ as functions of T^{-1} (fig. 7). By making a statistical linear regression analysis, ionization energies of $\Delta E_{no} = 553$ meV and $\Delta E_{po} = 641$ meV are obtained with standard deviations of 1 meV in both cases. In the temperature region where the measurements were performed, no field dependence of e_p^t was observed up to -30 V in agreement with previous results²²⁾. A possible field dependence was found for e_n^t at higher reverse voltages. However, for voltages up to -10V which have been used for our transient measurements the field dependence was negligible small for e_n^t .

In a previous paper, it has been shown²³⁾ that, for $q \cdot V_R \gg kT$ the steady state current $I_R^t(\infty)$ of a reverse-biased P-N junction in darkness is given by

$$I_R^t(\infty) = q \cdot A N_{TT} (W - W_0) \cdot \frac{e_n^t e_p^t}{e_n^t + e_p^t} \quad (14)$$

where W_0 is the outer parts of the transition region in which the net excitation rate can be neglected because of competing recombination processes due to free carrier tails extending from the neutral regions into the space charge region. Combining eq 14 with equations 10, 11 and 13 we obtain

$$\frac{I_R^t(\infty)}{\tau (W - W_0)} = F \cdot T^2 \cdot \exp \left[-(\Delta E_{no} + \Delta E_{po}) / kT \right] \quad (15)$$

where F is a temperature independent factor. Thus plotting $\log I_R^t(\infty) / (\tau (W - W_0) \cdot T^2)$ vs $1/T$ (fig. 7) information about the sum

$\Delta E_{no} + \Delta E_{po}$ is achieved without employing $I_R^t(0)$. From the slope of the straight line, a value of 1209 meV is obtained for $\Delta E_{no} + \Delta E_{po}$. The method used for the determination of $W - W_0$ has been described previously²²⁾. A plot of $W - W_0$ as a function of temperature for a reverse bias of -10V is shown in fig. 9.

Transient measurements are always difficult to perform and experimental errors can arise more easily than in steady-state measurements. An additional check of results obtained from transient measurements is therefore worthwhile. The steady-state dark current $I_R^t(\infty)$ was $1,27 \cdot 10^{-8}$ A at 303K. Using eq. 14 and the results presented in fig. 7, a value of $4 \cdot 10^{10} \text{ cm}^{-2}$ is calculated for the product $N_{TT} (W - W_0)$. Independent information about $N_{TT} (W - W_0)$ is, however, readily obtained by integrating the photo-current transients which are observed for photon energies smaller than half the band-gap²⁴⁾. The charge Q thus obtained is given by¹⁰⁾

$$Q = \frac{1}{2} qA \frac{e_p^o}{e_n^o + e_p^o} N_{TT} (W - W_0), \quad (16)$$

where e_n^o and e_p^o are the optical emission rates of electrons and holes for those photon energies which have been used for recharging the P+N junction¹⁰⁾. From these investigations a value of $4.2 \cdot 10^{10} \text{ cm}^{-2}$ is obtained for $N_{TT} (W - W_0)$, in good agreement with the results found from dark current measurement.

VII. Discussion

The sum of the thermal activation energies $\Delta E_{no} + \Delta E_{po}$ which has been obtained in section VI can be expected to be equal to E_{go}

at $T = 0\text{K}$ (fig. 1). Recent data published by Bludau, Onton and Heinke,⁹⁾ which, since they were taken with wavelength deviation techniques, are expected to be particularly accurate, give $E_{go} = 1195\text{ meV}$ in the temperature range 200-300K, where our transient measurements were performed. From the data of fig. 7, we obtain a value of 1194 meV for the sum of ΔE_{no} and ΔE_{po} which is in good agreement with the results of Bludau et al. In the temperature range 250-310K where the measurements presented in fig. 8 have been performed, E_{go} is about 1206 meV⁹⁾, which is very close to the value of 1209 meV obtained from the slope of the straight line presented in fig. 8. Comparing these results with tab. I it is seen that only the value reported by Parillo and Johnson are in reasonable agreement with our result. However, their values for ΔE_{no} and ΔE_{po} differ considerably from ours. Furthermore, the absolute values for e_p^t they quote are about one order of magnitude smaller than previously-published data and those presented in this paper.

The experimental results so far discussed give only information about the absolute zero energy values obtained from a linear extrapolation at higher temperatures. They are therefore not influenced by any temperature dependence of E_C , E_V or E_T as long as any higher-order temperature-dependence of the band-gap is neglected. For many purposes, only the real thermal ionization energies are of importance. These values, however, cannot be determined experimentally but have to be calculated from the temperature-dependence of E_C , E_V and E_T . From recent optical data¹²⁾, there are strong indications that the gold acceptor level

is pinned to the conduction band when the temperature is varied. This would imply that ΔE_n is independent of temperature, while ΔE_p has the same temperature dependence as the band gap. The band gap values obtained in reference 9) can be described by the semi-empirical expression proposed by Varshni²⁵⁾ to within about 1 meV in the temperature range 0-300K.

Hence, using

$$\Delta E_n (T) = \text{constant} = \Delta E_{no} \quad (16)$$

and

$$\Delta E_p (T) = \Delta E_p (0) - \frac{\alpha T^2}{1108+T} \quad (17)$$

where $\alpha = 7.02 \cdot 10^{-4}$ eV/K, the (not extrapolated) thermal ionization energies $\Delta E_n(0)$ and $\Delta E_p(0)$ can be estimated at $T = 0$ by putting expressions (16) and (17) above into eq. (10) and (11). Performing the same analysis as for the determination of ΔE_{no} and ΔE_{po} , the following values for the thermal ionization energies at zero temperature were found: $\Delta E_{no}(0) = \Delta E_{no} = 0.553$ eV and $\Delta E_p(0) = 0.613$ eV. Similar calculations can be made at all temperatures. The data at 0°K and 90°K are summarized in table II, together with values of ΔE_n^0 and ΔE_p^0 obtained from optical measurements. For comparison, the data from ref 9 for the band-gap are also included. It can readily be seen that there is good agreement between the thermal and optical ionization energies on one hand and the sum of $\Delta E_n + \Delta E_p$ and the band-gap on the other. Hence, even results from thermal measurements are not in contradiction to the conclusion that the gold acceptor impurity is

pinned to the conduction band when the temperature is changed, and that no relaxation is observed due to excitation processes from this level.

Moreover, the capture rate c_p^t of holes can be estimated from eq. 5 together with the value $N_{TT} = 3 \cdot 10^{15} \text{ cm}^{-3}$, giving a value of $8.2 \cdot 10^{-7} \text{ cm}^3/\text{s}$ at 77 K and $1.1 \cdot 10^{-7} \text{ cm}^3/\text{s}$ at 300 K. Inserting these results in eq. 2 together with the value of $A_p = 6.2 \cdot 10^{11} \text{ s}^{-1}$ (which has a standard deviation of about $0.3 \cdot 10^{11} \text{ s}^{-1}$) taken from fig. 7 and the density of states effective mass taken from Barber 26) we obtain $g_A \approx 3.2$. Such a determination of g_A cannot be very accurate. It shows, however, the consistency in our measurements because both the values of the capture cross-section and the degeneracy factor are in fair agreement with generally-accepted values²⁷⁾²⁸⁾ of the parameters for the gold acceptor level in silicon. Using a degeneracy factor $g_A = 3.2$ the capture rate c_n^t of electrons can be estimated from eq. 1 giving a value of $2 \cdot 10^{-8} \text{ cm}^3/\text{s}$ at 300 K. In tab. III this result is compared with previously published values of c_n^t and c_p^t . We believe that the disagreement in previously reported capture rates might in some cases arise from uncertainties in the determination of the gold acceptor concentrations.

In a recent letter⁷⁾, Parrillo and Johnson presented a new interpretation to bring available data of the gold acceptor level in silicon into consonance by assuming that the acceptor level at $T = 0 \text{ K}$ is 0.1 eV higher than previously reported and that the level shifted proportionally with the band gap using capture coefficients of Fairfield and Gokhale²⁸⁾ with temperature variations as reported by Bemski²¹⁾. In contrast to their results,

the experimentally-determined thermal emission rates used in this analysis are in agreement with earlier data ⁵⁾⁶⁾. Unlike in their case, our data also suggest that the energy distance of the gold acceptor level from the conduction band is independent of temperature ¹²⁾. This results in thermal activation energies, which are in good agreement with recent optical investigations ⁹⁾¹⁰⁾.

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Figure captions

- Fig. 1 Temperature-dependence of the band-gap in silicon.
- Fig. 2 Temperature-dependence of the total hole-mobility
(see text)
- Fig. 3 Photocurrent I_R^O versus the width W of the space
charge region of a P+N diode illuminated from the
N-side with strongly-absorbed light at different
temperatures.
- Fig. 4 Temperature-dependence of L_p^2 where L_p is the diffusion
length of holes.
- Fig. 5 The gold-doped P+N diode used for the measurements.
- Fig. 6 Typical dark current transient in (a) semilogarithmic
and (b) linear scale. All transients are exponential
over at least 1.5 decades.
- Fig. 7 Temperature-dependence of $\log(e_n^t \cdot T^{-2})$ and $\log e_p^t$.
The slope of the straight lines are equal to $\Delta E_{po}/2.3k$
and $\Delta E_{no}/2.3k$ respectively, the linearly-extrapolated
absolute zero thermal activation energies.
- Fig. 8 Logarithm of the reverse dark-current $I_R^t(\infty)$ corrected
with the pre-exponential temperature dependence of
eq. 15 versus T^{-1} . From the slope of the straight line,

the linearly-extrapolated absolute zero sum of the two thermal activation energies is obtained.

Fig. 9

Temperature-dependence of the effective space-charge region.

Table captions

Table I: Published data on the energy position of the gold-acceptor level in silicon.

Table II: Comparison between optical and (not extrapolated) thermal ionization energies ΔE^O and ΔE^t respectively.

Table III: Published data on capture rates of electrons c_n^t and holes c_p^t for the gold-acceptor level in silicon.

$E_C - E_{Au}$ [meV]	$E_{Au} - E_V$ [meV]	$(E_C - E_{Au})$ + $(E_{Au} - E_V)$ [meV]	Tempera- ture range of measure- ments [K]	E_{go} [meV]	Author	Method	Ref
540^{+20}	620^{+20}	1160^{+40}	200-330	1195	G B Collins et al	Halleffect and resistivity	1
540^{+20}			93-373		B I Boltaks et al	Halleffect and resistivity	2
	570		220-300		C T Sah and A F Tasch	Photocurrent transient	3
545^{+5}			200-260		R R Senechal and J Basinski	Capacitance	4
547^{+2}	589^{+2}	1136^{+4}	200-300	1195	C T Sah et al	Dark current transient	5
$545^{+1.4}$	$588^{+1.3}$	1133^{+3}	200-300	1195	A F Tasch and C T Sah	Photocurrent transient	6
490^{+20}	720^{+10}	1210^{+30}	310-370	≥ 1206	L C Parillo and W C Johnson	Dark current (transients)	7
582					L D Yau and C T Sah	Dark capacitance transients	8
553	641	1194	200-300	1195	This paper	Dark current transients	

TABLE I

T [K]	ΔE_n^t [meV]	ΔE_p^t [meV]	$\Delta E_n^t + \Delta E_p^t$ [meV]	ΔE_n^O [meV]	ΔE_p^O [meV]	$\Delta E_n^O + \Delta E_p^O$ [meV]	E_g [meV]
0	553	613	1166				1170 ⁹⁾
90	553	609	1162	555 ¹⁰⁾	610 ¹⁰⁾	1165	1166 ⁹⁾

TABLE II

Author	Capture rates (300 K)		Ref
	c_n^t [cm ³ /s]	c_p^t [cm ³ /s]	
Bemski	$5 \cdot 10^{-9}$	$1 \cdot 10^{-8}$	21
Davis	$3 \cdot 10^{-8}$ (77 K)		29
Fairfield and Gokhale	$1.65 \cdot 10^{-9}$	$1.15 \cdot 10^{-7}$	28
This paper	$2 \cdot 10^{-8}$	$1 \cdot 10^{-7}$	

TABLE III

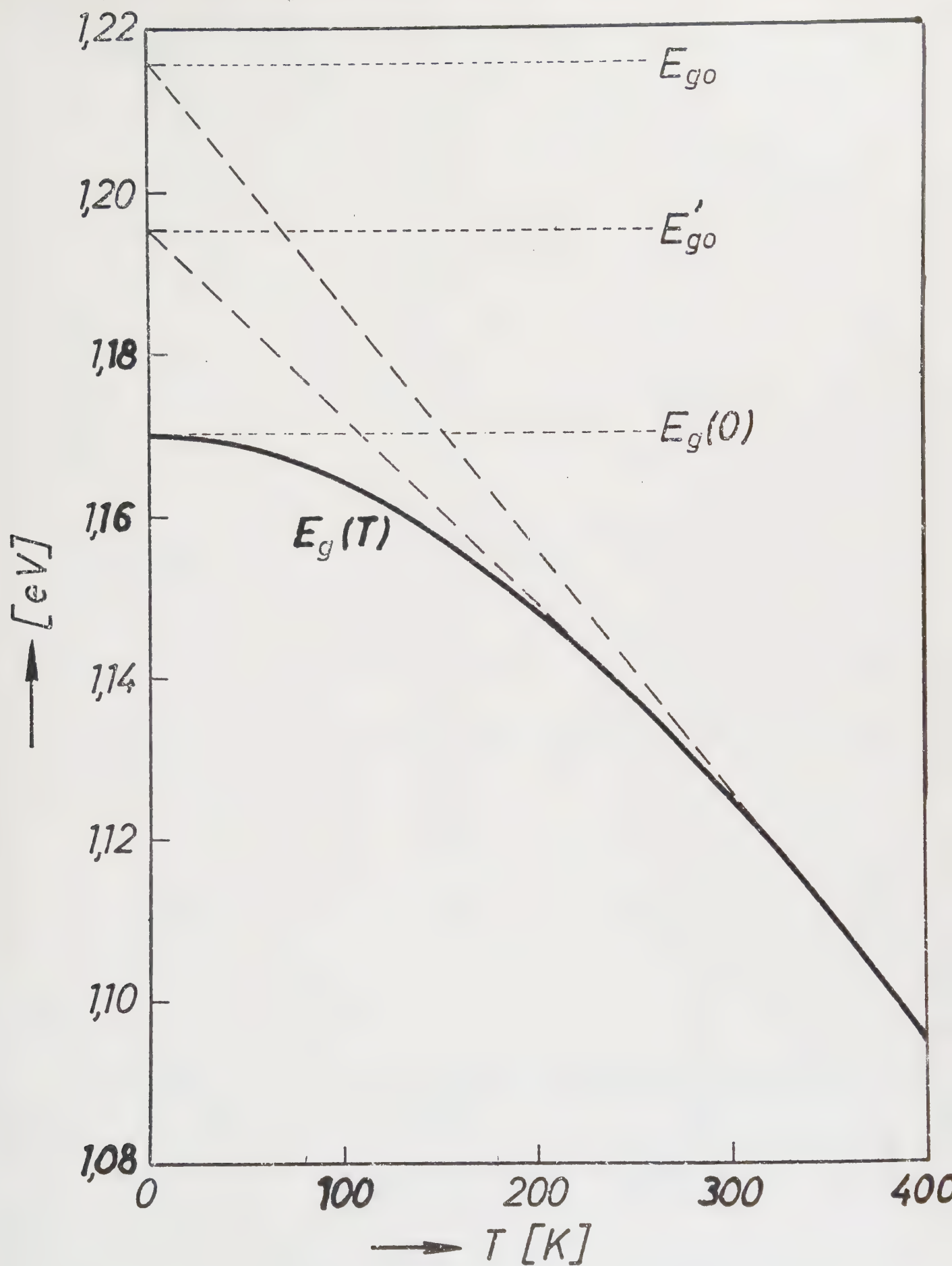


Fig.1

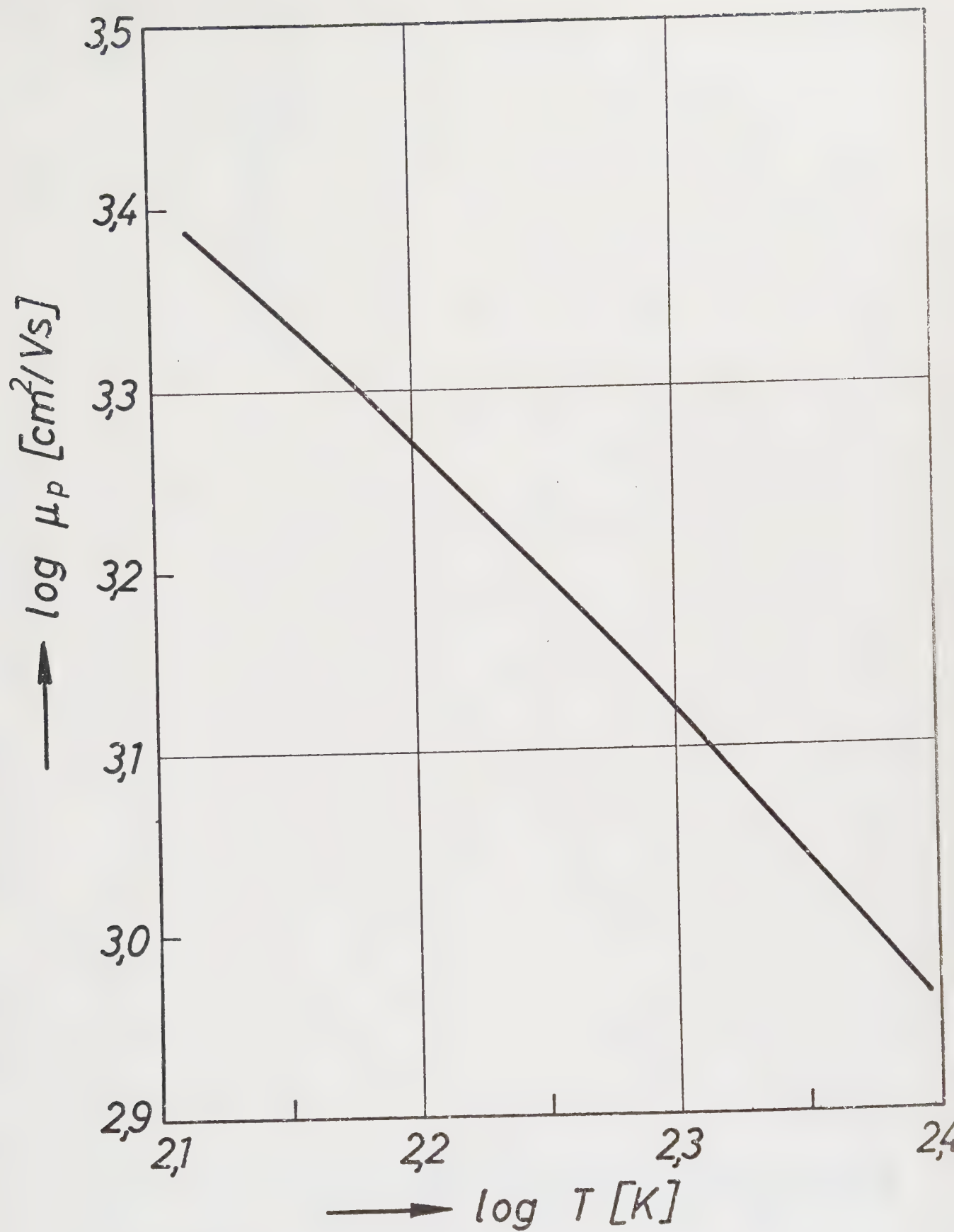


Fig. 2

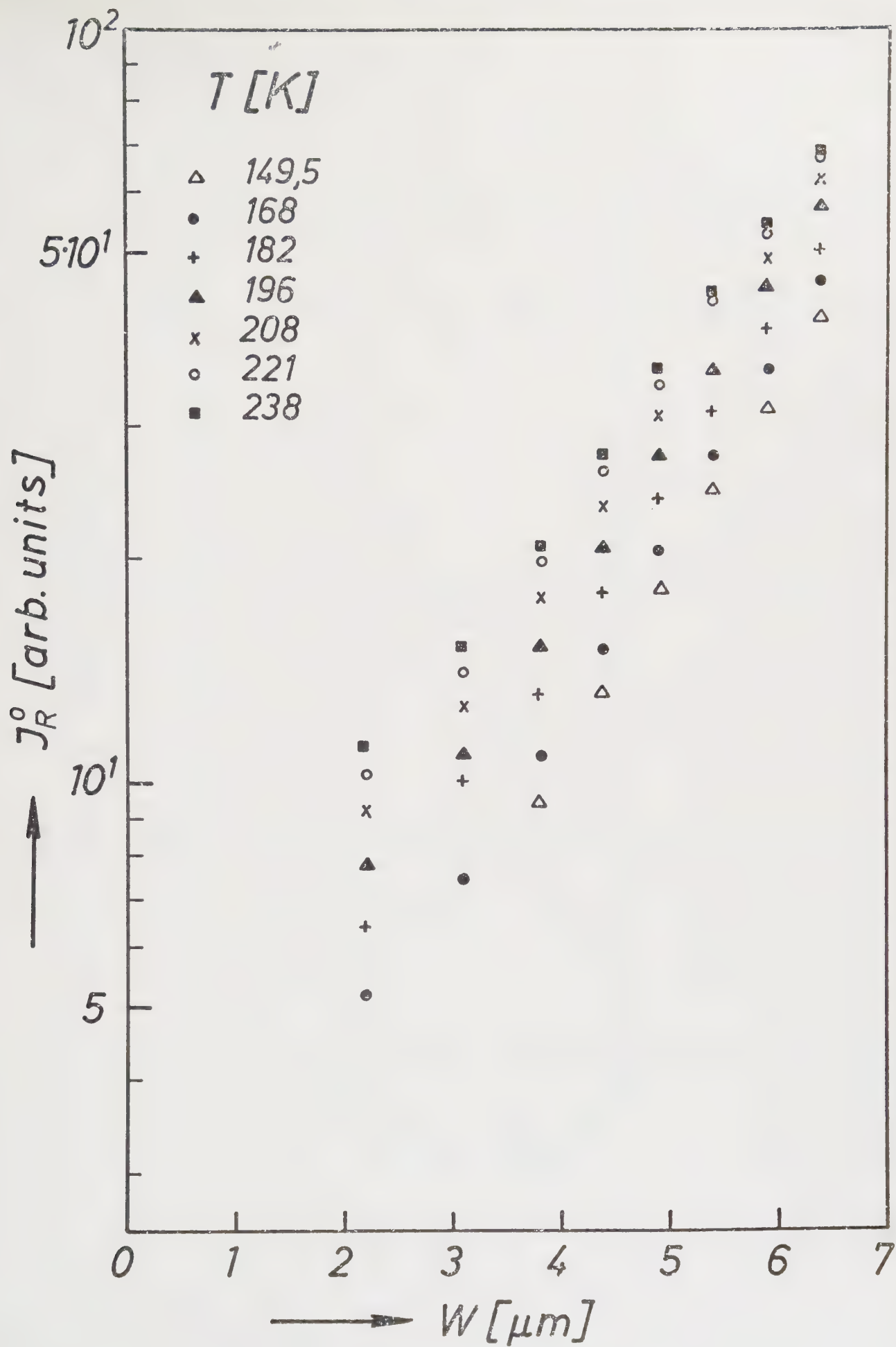


Fig.3

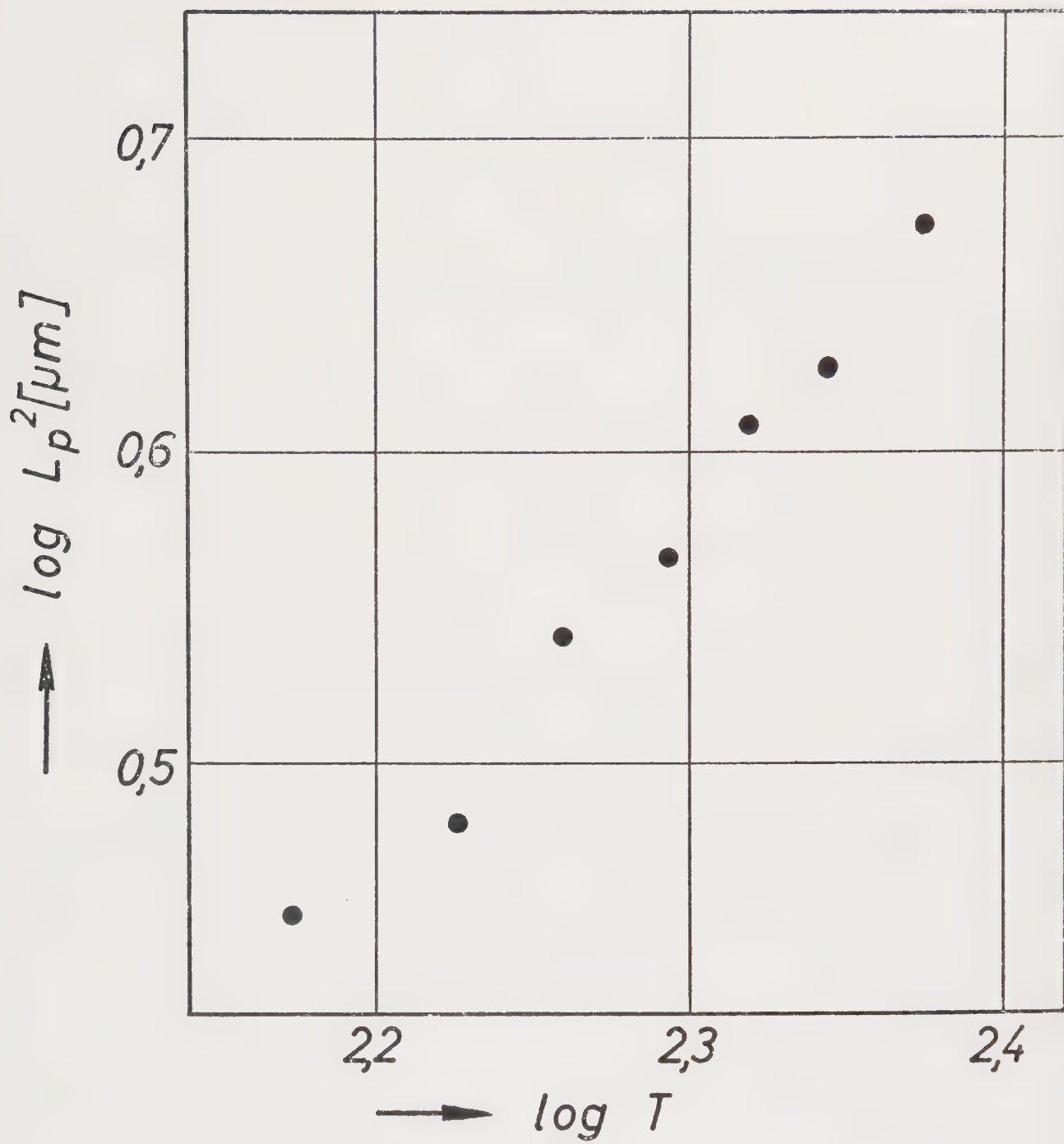


Fig. 4

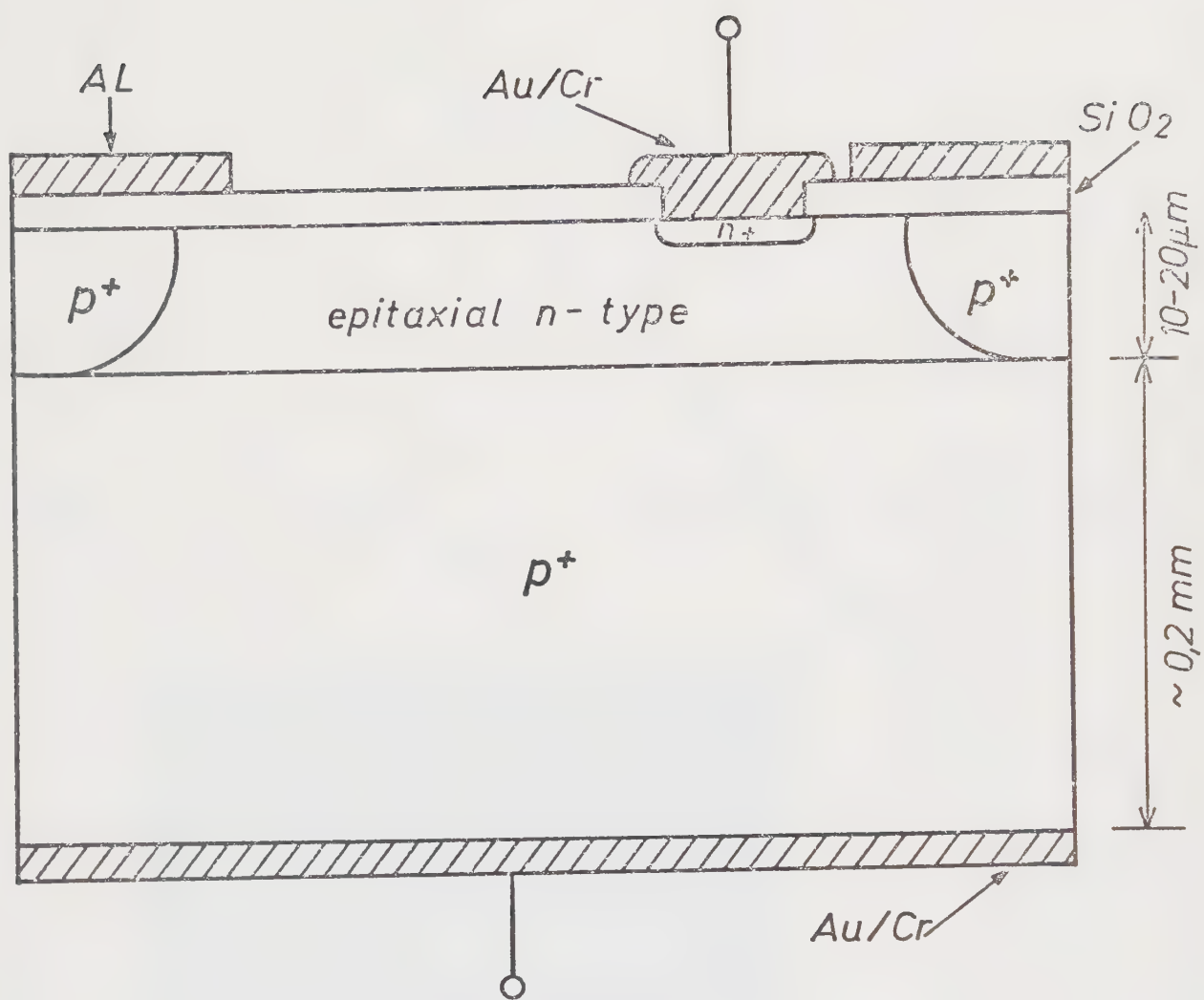


Fig.5

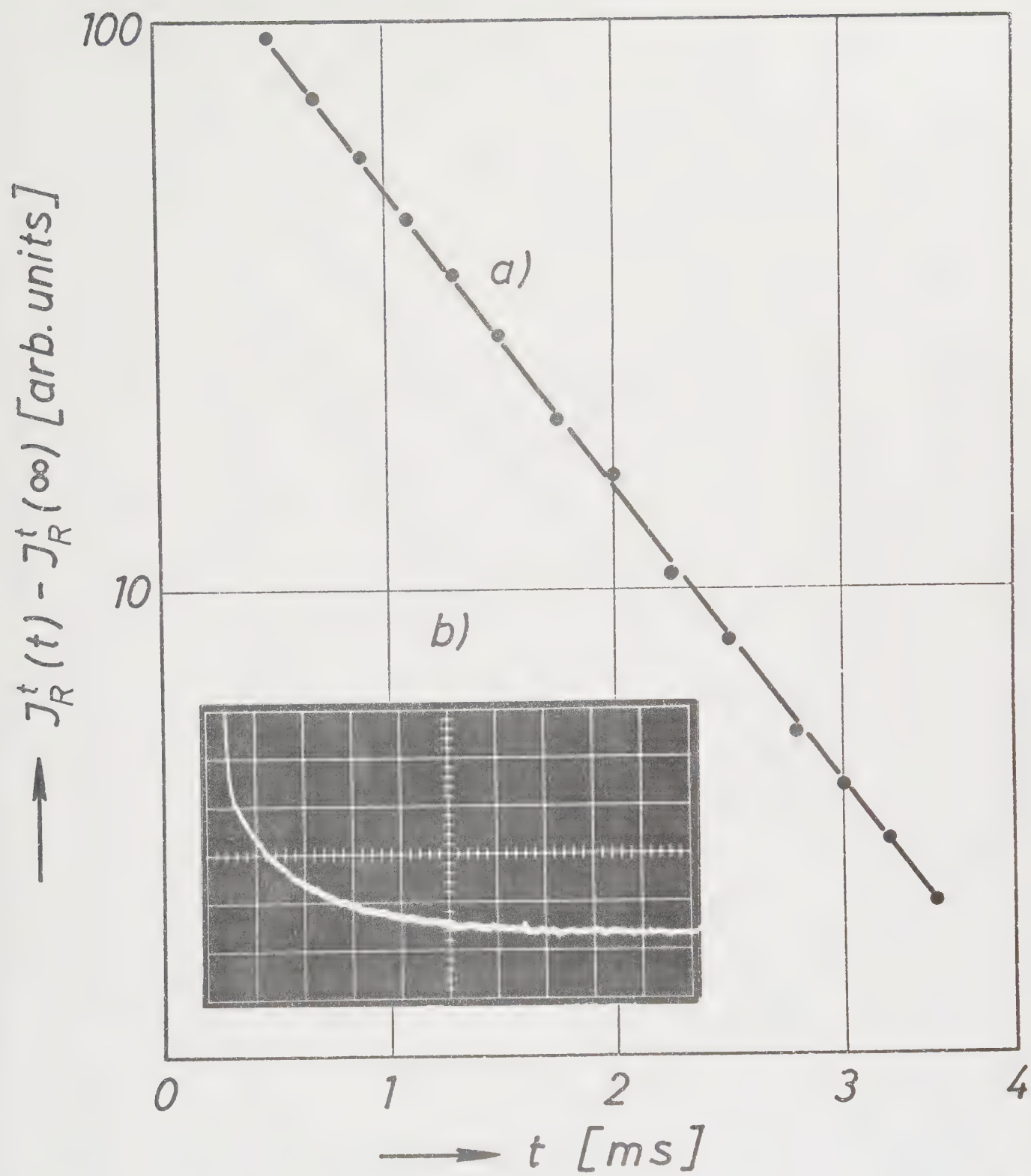


Fig.6

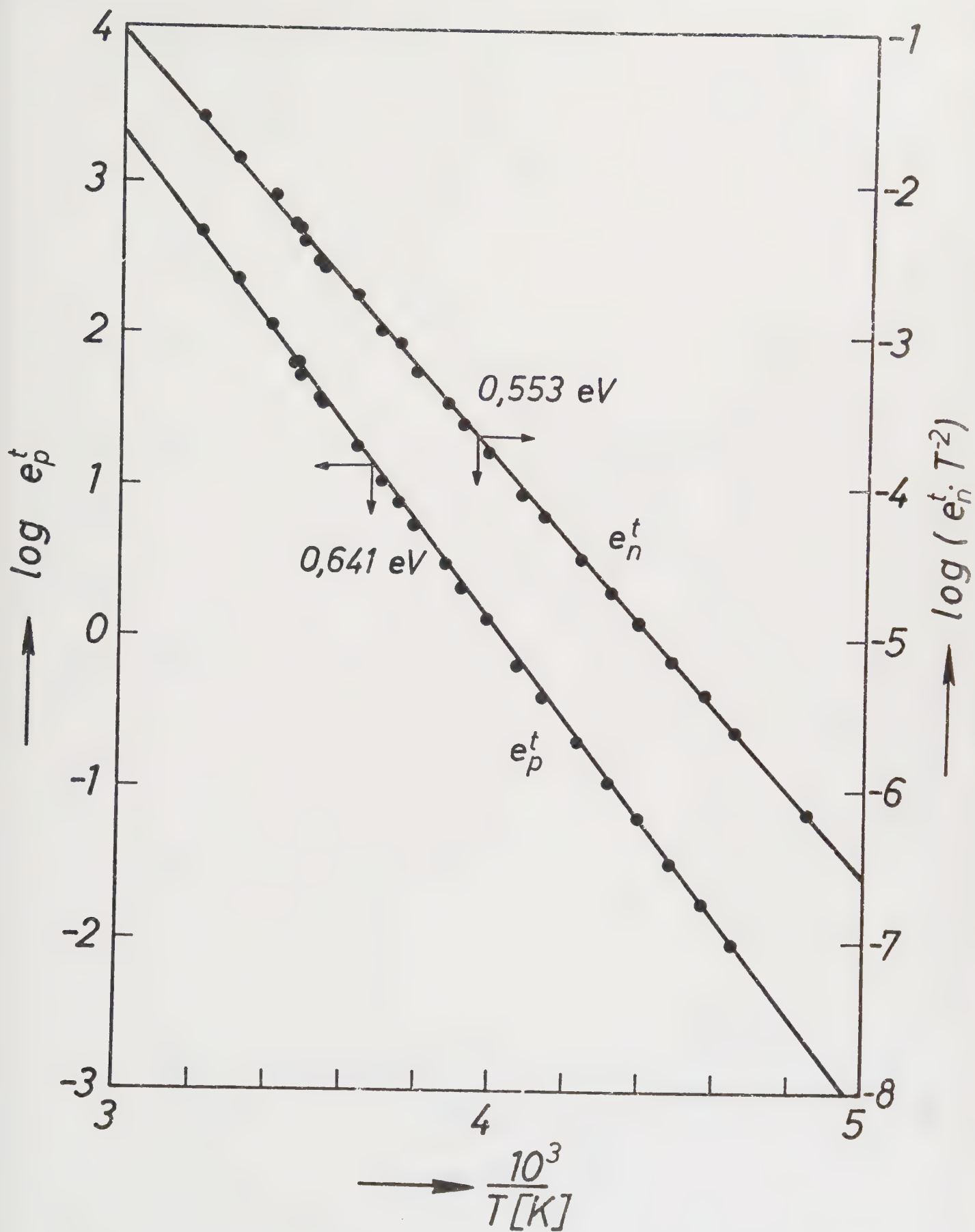


Fig. 7

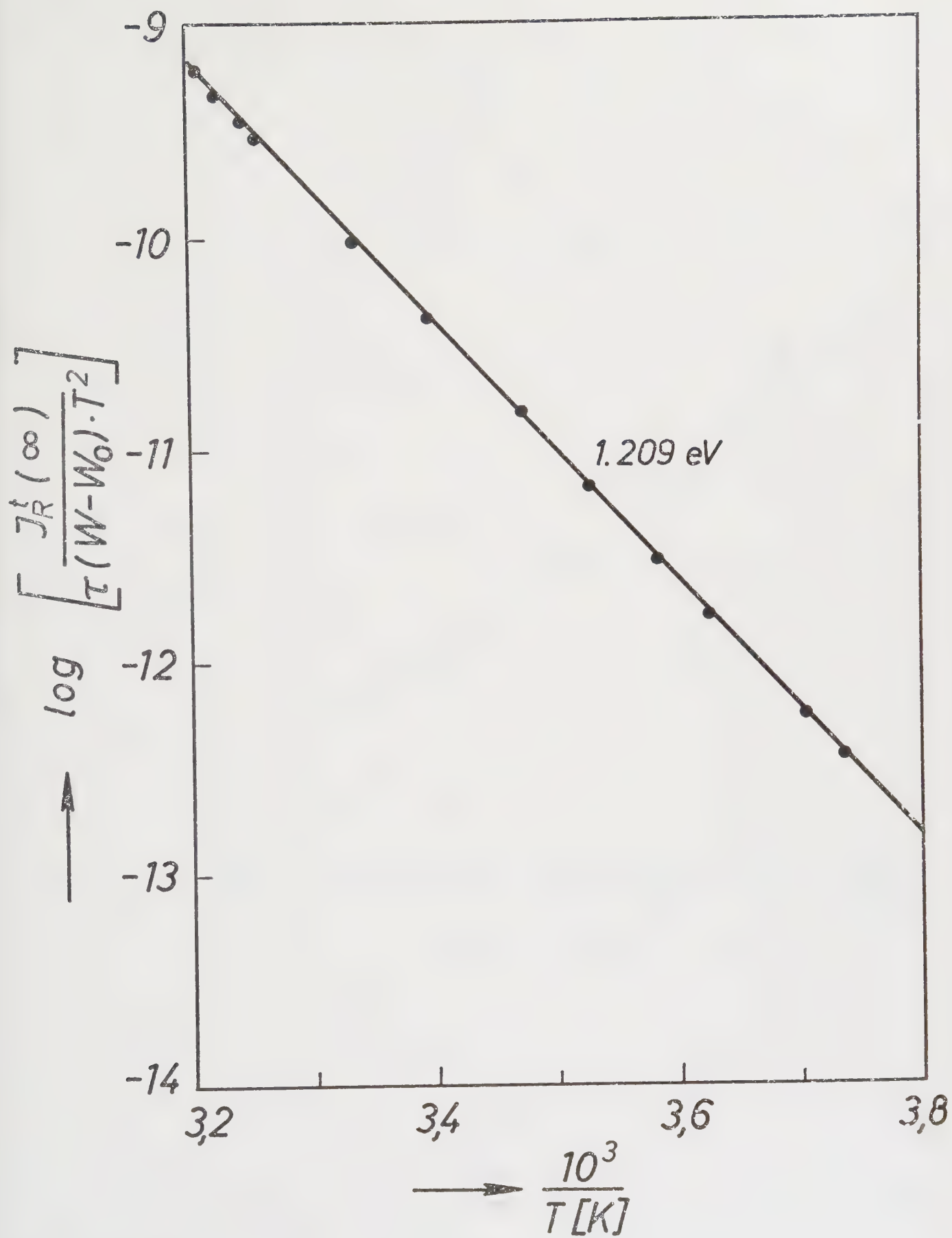


Fig.8

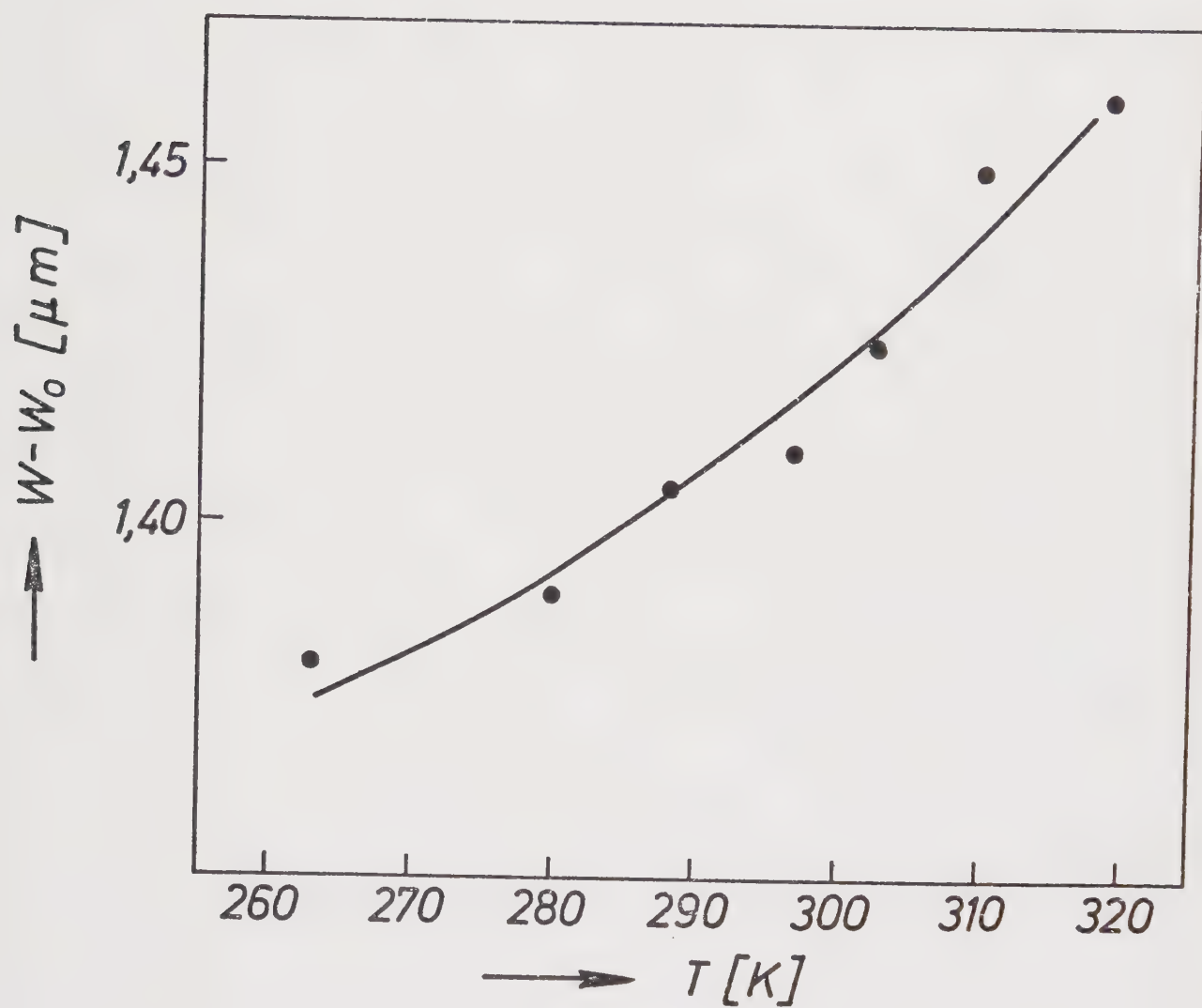


Fig. 9

The role of displacement currents in deep impurity induced
PN-junction transients

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Abstract

When measurements of PN-junction current transients are used for the investigation of deep impurities in semiconductors, not all the charge created in the space charge region contributes to current transients in the outer circuit. Part of the charge is used to neutralize that region in which the space charge region decreases during the excitation process. It is shown that the fraction of the charge totally created which traverses the outer circuit is dependent on the energy position of the deep impurity, on the reverse voltage and on the experimental starting conditions. Interpretation of transient data therefore depends strongly on these parameters.

The role of displacement currents in deep impurity induced PN-junction transients

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1. Introduction

Photocurrent and photocapacitance measurements have been a powerful tool for the study of impurities in many semiconductors. These new techniques allow the deep impurity levels within the space charge region of a PN-junction ¹⁻⁵⁾ or Schottky barrier ⁶⁾ to be studied directly. Often, concentrations, emission rates for electrons and holes and the energy level positions are deduced from current transients. The slow current transients consist of three parts: electron and hole generation currents and displacement current due to the change of the electric field in the transition region caused by the time dependence of the trapped charge. The current measured in the external circuit is the sum of these three components. This implies for a one-sided P⁺N junction that the galvanic current due to electron transport is met by a displacement current in the opposite direction which reduces the former current by a factor D. This factor therefore is of considerable importance in the study of deep levels in semiconductors using transient current measurements. Although the importance of D is widely accepted, there is considerable disagreement among different authors as to its value. In some cases ¹⁻³⁾, D has been taken to be 1, whereas,

in other cases ^{4,5)}, D has been assumed to be 2. In ref 7, the factor D was established from independent measurements. A value of 2 is easily calculated if free-carrier tails extending from the neutral regions into the space-charge region are neglected. In this paper, however, it will be shown that the factor D depends on both the energy position of the deep impurity level and the concentration of the shallow background doping due to free-carrier tails extending into the space-charge layer. For a one-sided step junction with a homogeneous concentration of deep levels, D is found to take any value greater than 1 depending on the experimental conditions. This is of vital importance in the determination of emission rates and concentration profiles and may produce large errors when values of 1 or 2 are assumed for D. Finally, an experimental method to measure D-values for any particular case is presented.

2. D-factor

The following considerations are made for a one-sided P⁺N step junction, in which the width of the negative space charge region can be neglected. A homogeneous concentration of deep energy levels in the upper half of the bandgap is assumed. It can easily be shown that similar results are obtained for a N⁺P junction. It has recently been established ⁸⁾ that if the concentration of deep energy levels is small compared with that of the shallow background doping, net excitation processes can only be achieved in a region W-W₀ within the space charge layer. Denoting the boundaries of the region W-W₀ by x₁ and x₂ (figure 1), the free hole concentration at x₁ is given by ⁸⁾

$$p = n_1 \frac{\tau_{po}}{\tau_{no}} + p_1 \quad (1)$$

and the free electron concentration at x_2 by

$$n = \frac{\tau_{p0}}{\tau_{no}} n_1 + p_1 \quad (2)$$

where τ_{p0} and τ_{no} are the majority carrier lifetimes for holes and electrons respectively and the quantities n_1 and p_1 are defined by

$$n_1 = N_C \cdot \exp \left(- \frac{E_C - E_T}{kT} \right) \quad (3)$$

$$p_1 = N_V \cdot \exp \left(- \frac{E_T - E_V}{kT} \right) \quad (4)$$

N_C and N_V in these expressions are the effective density of states in the conduction and valence bands respectively.

Hence, if $n_1 \gg p_1$ and $\tau_{no} \approx \tau_{p0}$, x_1 corresponds to a position in the space charge region at which the distance from the quasi-Fermi level for holes to the valence band edge is $E_C - E_T$ (figure 1). By similar considerations, it can be shown that x_2 corresponds to a position at which the quasi-Fermi level for electrons coincides with the deep energy level. Starting from a condition with all deep energy levels in the region $W-W_0$ occupied, it is readily shown that, when all deep levels are completely emptied by thermal or optical excitation of electrons into the conduction band, the positive charge in the space charge region has increased by an amount

$$Q_T = q A (W-W_0) N_{TT} \quad (5)$$

where q is the electron charge, A is the diode area and N_{TT} is the total concentration of the deep energy levels. Keeping the reverse bias constant, the width of the positive space charge region will then decrease. This implies that some of the electrons which are excited in the region $W-W_0$ will be used to neutralize the outer part of the positive space charge region. Denoting this charge by Q_0 , the rest of the charge is $Q_T - Q_0$,

will pass through the external circuit and increase the negative space charge region on the P-side. Hence, defining a factor

$$D = \frac{Q_T}{Q_T - Q_0} \quad (6)$$

as the ratio between the excited charge Q_T within the effective space charge region $W-W_0$ and the experimentally measured negative charge Q_T-Q_0 in the external circuit, it follows from eqns 5 and 6 that

$$Q_{Cn} = Q_T - Q_0 = -\frac{1}{D} q A (W-W_0) N_{TT} \quad (7)$$

If, on the other hand, all deep energy levels are initially empty and are then filled by electrons from the valence band, the positive space charge will decrease by an amount Q_T given by eqn 5. Due to the electric field, this positive charge is pushed to the P-side of the junction where an amount $Q_T - Q_0$ is needed to neutralize the outer part of the negative space charge region. The rest of the holes, comprising a charge Q_0 , will pass through the external circuit to neutralize the increase of the positive space charge region. The ratio between the excited charge in the region $W-W_0$ and the measured charge no W becomes

$$\frac{D}{D-1} = \frac{Q_T}{Q_0} \quad (8)$$

Together with eqn 5, we therefore obtain for the measured positive charge Q_{Cp} in the external circuit

$$Q_{Cp} = \left(1 - \frac{1}{D}\right) q A (W-W_0) N_{TT} \quad (9)$$

Because the concentration of deep energy levels is assumed to be small compared with the shallow doping, a change of the occupancy of the deep levels in the space charge region will only cause a small variation in the width of the space charge layer. Hence, the charge Q_0 is distributed

in a very narrow region close to x_n causing an electric field contribution $E'(x)$ which can be taken as constant all over the positive space charge region (figure 2a) and is given at x_n by

$$E'(x_n) = - \frac{Q_0}{\epsilon \epsilon_0} . \quad (10)$$

At the end of the excitation, the charge Q_0 has been neutralized and a new charge Q_T has been created in the region $W-W_0 = x_2 - x_1$ causing a field at x_1 (figure 2b) which can be written as

$$E''(x_1) = - \frac{Q_T}{\epsilon \epsilon_0} . \quad (11)$$

Due to the one-sided step junction, almost all of the reverse bias is taken up by the positive space charge layer. For a constant reverse bias we therefore obtain

$$E'(x_n) x_n = \frac{1}{2} E''(x_1)(x_2 - x_1) + E''(x_1)x_1 . \quad (12)$$

Inserting eqn 10 and 11 in eqn 12 gives

$$\frac{Q_0}{Q_T} = \frac{x_2 + x_1}{2 x_n} . \quad (13)$$

Together with eqn 6 or 8 we then obtain

$$D = \left(1 - \frac{x_2 + x_1}{2 x_n} \right)^{-1} . \quad (14)$$

From eqn 14 it is obvious that D depends on the ratio between the effective space charge region $W-W_0$ and the width of the positive space charge region. Because $W-W_0$ depends among other factors on the energy of the deep level E_T and the reverse bias V_R , the factor D is a function of both E_T and V_R . It is readily shown that $x_2 + x_1$ never exceeds x_n under the experimental conditions discussed so far if $E_C - E_T$ is larger than $E_C - E_{Fn}$ in the neutral N-region. This means that D can take values

between 2 and 1 depending on E_T and V_R .

In eqn 14, the boundaries x_1 and x_2 of the effective space charge region are established by the equilibrium conditions of eqn 1 and 2. An experimental situation is however often found in which a reverse voltage V_R is applied, all the deep levels are emptied, the reverse voltage is lowered to a value V_{R0} and after that reestablished to the value V_R . The charge captured by the deep levels is now kept in a region $x_2 - x_{20}$ where x_{20} corresponds to the reverse voltage V_{R0} . If this charge is emitted, the D-factor is given by

$$D = \left(1 + \frac{x_2 + x_{20}}{2 x_n} \right)^{-1} \quad (15)$$

The sum $x_2 + x_{20}$ might approach the value $2x_n$ and the D-factor can therefore in this situation take any value larger than 1. This case occurs when transient charge flows are used for concentration profiling.

3. Theoretical determination of the D-factor

In this section we will estimate the influence of the energy position of the deep impurity and the reverse voltage on the D-factor. To begin with, we consider an abrupt P^+N -junction with a homogeneous doping of deep impurities with an energy level at E_T . Starting with the familiar expression for the potential $\phi(x)$ on the N-side of an abrupt P^+N -junction

$$q \phi(x) = \frac{q N_d}{\epsilon \epsilon_0 \cdot 2} (x_n - x)^2 \quad (16)$$

where N_d is the concentration of shallow-donors and ϵ is the dielectric constant of the material, the values of x_1 and x_2 can be calculated by using the conditions of eqn 1 and 2. One finds for the two parameters

$$x_2 = x_n - \left\{ \frac{2\epsilon\epsilon_0}{q N_d} \left[E_{Fn} - E_T - kT \ln \left(1 + \frac{p_1}{n_1} \frac{\tau_{no}}{\tau_{po}} \right) \right] \right\}^{1/2} \quad (17)$$

and

$$x_1 = x_n - \left\{ \frac{2\epsilon\epsilon_0}{q N_d} \left[q(V_R + V_D) - (E_T - E_{Fp}) + kT \ln \left(1 + \frac{n_1}{p_1} \frac{\tau_{po}}{\tau_{no}} \right) \right] \right\} \quad (18)$$

Calculations have been made for a silicon diode at a temperature of 100 K with $N_d = 5 \cdot 10^{15} \text{ cm}^{-3}$ and $N_a = 5 \cdot 10^{18} \text{ cm}^{-3}$. In fig 3, the ratios x_1/x_n and x_2/x_n are given as functions of the energy position of the deep impurity level for different reverse voltages. As can be seen, the effective space charge region decreases with increasing depth of the impurity. The corresponding values of the D-factor are shown in fig 4 and in fig 5 the influence of reverse voltage on the D-factor is shown for different energy positions of the deep impurity. A corresponding calculation of the x_1 and x_2 -values has been made in ref 8 for a PN-junction containing a low concentration of gold impurities with linearly shallow doped N-side with a doping gradient of $1.68 \cdot 10^{19} \text{ cm}^{-4}$ and a homogeneously shallow doped P-side with $N_a = 5 \cdot 10^{18} \text{ cm}^{-3}$. The theoretical D-value in this case is shown as a function of reverse bias in fig 6.

Up to this point, an experimental condition has been considered in which all the deep impurity levels between the x_1 and x_2 -points in the space charge region are filled before the excitation. As mentioned above, the excited charge can be contained in a region $x_2 - x_{20}$ close to the outer part of the space charge region by emptying all deep levels at a voltage V_R and refilling the region $x_2 - x_{20}$ by lowering the voltage to a value V_{R0} . To illustrate the variation of the D-factor in this case, a theoretical curve is shown in fig 7 for the same diode as in fig 6. The value of V_R is kept at 10 V and the x_2 and x_{20} values corresponding to

different V_{R0} are taken from ref 8.

4. Experimental determination of the D-factor

In the experimental determination of the D-factor, the PN-junction is first reverse biased to a certain voltage V_R . The temperature is low enough for thermal processes to be neglected and the diode is illuminated with a photon energy capable of emptying all the deep impurity levels inside the effective space charge region. This is the starting situation, which is followed by a lowering of the reverse voltage to a value V_{R0} . The voltage is then brought back to the value V_R and a situation has now been reached in which the deep levels have been filled within a fraction of the space charge region. Upon illuminating the diode again, excitation takes place in the region x_2-x_{20} defined in section 3. This excitation causes the transport of a charge Q_C in the outer circuit, which can be measured as a current transient, with

$$Q_C = \int_0^{\infty} J_R(t) dt \quad (19)$$

When the deep impurities are emptied, the space charge region decreases slightly. The charge Q_0 needed to neutralize this part can be measured by increasing the reverse voltage to a value at which the space charge region takes the same value as before the excitation. This charge is created by removing free carriers when the space charge region is increased and, because $Q_T = Q_C + Q_0$, the D-factor is easily obtained from

$$D = \frac{Q_C + Q_0}{Q_C} \quad (20)$$

For energy levels close to the middle of the energy gap, not only electrons but also holes will be excited. In this case, the current in

the external circuit does not vanish when the steady state is reached. As shown in the appendix, the factor D is then determined by the relation

$$D = \frac{Q_{tr} + Q_0 + [J_R(\infty) - J_{R0}(\infty)] \tau}{Q_{tr} + [J_R(\infty) - J_{R0}(\infty)] \tau} \quad (21)$$

where τ is the time constant of the transient component, $J_R(\infty)$ and $J_{R0}(\infty)$ are the steady state currents in the external circuit before and after the reverse bias has been varied and Q_{tr} is defined by $Q_{tr} = \int_0^{\infty} (J_R(t) - J_R(\infty)) dt$, which is the charge contained under the current transient (shaded region in fig 8).

The D-factor was experimentally determined for P^+N silicon diodes doped with gold and used in previous investigations⁷⁾⁸⁾¹¹⁾. Their doping data correspond to the theoretical curves of fig 6 and 7. The experiments were performed at a temperature low enough to neglect thermal excitation processes. When the diode is illuminated with photon energy in the region 0.55 - 0.65 eV the electron occupancy factor of the gold acceptor level is lowered. From the transient photocurrent the parameters Q_C , $J_R^0(\infty)$ and $J_{R0}^0(\infty)$ were determined. The value of the D-factor was calculated using eq(21) by keeping $V_R = 10V$ and varying V_{R0} in the region 0 - 8V. The result is for comparison plotted together with the theoretical curve in fig 7.

5. Importance of the D-factor for the determination of emission rates and concentration profiles

It is shown above that the D-factor depends on the experimental conditions and may in principle take any value larger than one. This is not always realized when for example emission rates are calculated from transient current measurements. Using eq (7) and (9) the time dependence of the total current $J_R(t)$ which is observed in the external circuit due to excitation processes in the space charge region can be written as

$$J_R(t) = q A W_{\text{eff}}(t) \left[\frac{1}{D} U_n(t) + \left(1 - \frac{1}{D}\right) U_p(t) \right] \quad (22)$$

where U_n and U_p are the net rates of electron and hole emission from the deep energy levels and W_{eff} is the effective generation region. Because within the effective generation region W_{eff} recombination processes can be neglected, U_n and U_p are given by

$$U_n(t) = e_n n_T(t) \quad (23)$$

$$U_p(t) = e_p [N_{TT} - n_T(t)] \quad (24)$$

where e_n and e_p are the emission rates of electrons and holes respectively and n_T is the density of occupied deep energy levels.

Realizing that

$$\frac{dn_T}{dt} = U_p - U_n \quad (25)$$

and using eq (23) and (24) together with the boundary condition $n_T(0) = N_{TT}$, eq (22) can be rewritten as

$$J_R(t) = qAW_{\text{eff}}(t)N_{\text{TT}} \left[\left(1 - \frac{1}{D}\right)e_p + \left(\frac{e_p}{e_n + e_p} + \frac{e_n}{e_n + e_p} \exp\left(-\frac{t}{\tau}\right)\right) \cdot \left(\frac{1}{D}e_n - \left(1 - \frac{1}{D}\right)e_p\right) \right] \quad (26)$$

where

$$\tau^{-1} = e_n + e_p. \quad (27)$$

For concentrations of deep energy levels small compared with the density of shallow impurity levels, the time dependence of W_{eff} can be neglected. We then obtain from eqn (26)

$$\frac{e_n}{e_p} = D \frac{J_R(0)}{J_R(\infty)} - 1 \quad (28)$$

Hence, by measuring $J_R(0)$ and $J_R(\infty)$ and determining the time constant τ , both the emission rate of electrons and holes can be calculated using eqn (27) and (28) if the proper D-factor is used. D, however, depends on the experimental conditions and large errors might therefore arise when a constant value of $D = 1$ or 2 is used for the calculation of e_n and e_p .

Another example in which D plays an important role is in the determination of concentration profiles using transient current measurements. This is readily demonstrated for the case when hole excitation processes can be neglected. Q_T is then given by $qN_{\text{TT}}R$, where R is the volume within the space charge layer throughout which the net excitation occurs. Using eqn (19), the concentration of deep energy levels within a certain volume of the sample can readily be calculated from the expression

$$N_{\text{TT}}(x) = \frac{D}{qR} \int_0^{\infty} J_R(x,t) dt \quad (29)$$

This shows again that substantial errors might arise in the determination of concentrations if the D-factor is not carefully evaluated⁹⁾.

6. Conclusion

When making measurements of deep impurity induced current transients in PN-junctions, the current created through the excitation from deep levels is decreased by an oppositely directed displacement current. It has been shown in this paper that this greatly influences the interpretation of transient data. Depending on the exact details of the experimental situation, the ratio between these two current components can vary over a very wide range. These considerations become especially important when transient charge flows are used for concentration profiling. The effective generation region is then comprised by a very narrow region close to the outer part of the space charge region and large errors might arise if the D-factor is assumed to have a value of 1 or 2 in such measurements⁹⁾. Because the D-factor is also dependent on reverse voltage, care should be taken when transient measurements are used to obtain field dependences of emission rates in PN-junctions.

Acknowledgement

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Appendix: Calculation of the D-factor in the case of a center lying
close to the middle of the energy band gap

When two step excitation via a deep center cannot be avoided a current transient of the form shown in fig 8 is found with a steady state current $J_R(\infty)$. The charge Q_{tr} contained in the transient part is defined by

$$Q_{tr} = \int_0^{\infty} (J_R(t) - J_R(\infty)) dt. \quad (A1)$$

From eqn (23)

$$J_R(\infty) = K \frac{e_n e_p}{e_n + e_p} N_{TT} \quad (A2)$$

where $K = qAW_{eff}$ and $W_{eff} = W - W_0$ is assumed to be time independent.

This gives

$$J_R(t) - J_R(\infty) = KN_{TT} \left(\frac{e_n}{D} - \frac{e_n e_p}{e_n + e_p} \right) \exp\left(-\frac{t}{\tau}\right) \quad (A3)$$

and Q_{tr} is found from eqn (A1) :

$$Q_{tr} = KN_{TT} \frac{1}{D} \frac{e_n}{e_n + e_p} - KN_{TT} \frac{e_n e_p}{e_n + e_p} \tau \quad (A4)$$

In the deduction of eqn (26) it was assumed that $n_T(0) = N_{TT}$ and from eqn (A2) it can be understood that $n_T(\infty) = N_{TT}e_p/(e_n+e_p)$. This implies that the total change of charge Q_T in the space charge region is

$$Q_T = K (n_T(0) - n_T(\infty)) = KN_{TT} \frac{e_n}{e_n + e_p} \quad (A5)$$

Eqn (A4) therefore can be written as

$$Q_{tr} = \frac{1}{D} Q_T - J_R(\infty) \tau \quad (A6)$$

The charge Q_0 is related to Q_T by eqn (6) and the D-factor is given by

$$D = \frac{Q_{tr} + Q_0 + J_R(\infty) \tau}{Q_{tr} + J_R(\infty) \tau} \quad (A7)$$

Eqn (A7) is valid when carriers are excited in the entire effective space charge region. When excitation takes place in a fraction $x_2 - x_{20}$ of the space charge region, $J_R(\infty)$ in eqn (A7) shall be replaced by $J_R(\infty) - J_{R0}(\infty)$, where $J_R(\infty)$ and $J_{R0}(\infty)$ represent the steady state currents created in the regions $x_2 - x_1$ and $x_{20} - x_{10}$ respectively. In this case the D-factor therefore can be expressed by

$$D = \frac{Q_{tr} + Q_0 + [J_R(\infty) - J_{R0}(\infty)] \tau}{Q_{tr} + [J_R(\infty) - J_{R0}(\infty)] \tau} \quad (A8)$$

which is eqn(21).

Figure captions

- Fig 1 Band diagram of the P^+N -junction
- Fig 2 Schematic illustration of charges involved in the excitation process and corresponding field contributions in the space charge region. In a) Q_0 is the charge in the outer part of the depletion region which becomes neutralized by a fraction of $-Q_T$ in b) during the excitation process.
- Fig 3 The theoretical ratios x_1/x_n and x_2/x_n as functions of the deep energy level for different values of reverse voltage. The calculation is made for an abrupt P^+N -junction with $N_d = 5 \cdot 10^{15} \text{ cm}^{-3}$, $N_a = 5 \cdot 10^{18} \text{ cm}^{-3}$ and $\tau_{no}/\tau_{po} = 1$.
- Fig 4 The theoretical D-value of an abrupt P^+N -junction as a function of energy position of the deep energy level for different values of reverse voltage. Same doping is assumed as in the case of fig 3.
- Fig 5 The theoretical D-value of an abrupt P^+N -junction as a function of reverse voltage for different energy positions of the deep energy level. Same doping is assumed as in the case of fig 3.

- Fig 6 Theoretical D-value as a function of reverse voltage of a gold doped P^+N -junction with a linear shallow doping on the N-side. The values of x_1 and x_2 used in the calculation are taken from ref 8.
- Fig 7 Theoretical (solid curve) and measured (points) D-value when excitation is made in a fraction of the total effective space charge region of a gold doped P^+N -diode with linear N-side. The starting reverse voltage is 10V and the D-factor is given for different values of V_{R0} (see text).
- Fig 8 Current transient in the case of a center lying close to the middle of the energy band gap when two step excitation processes cannot be avoided.

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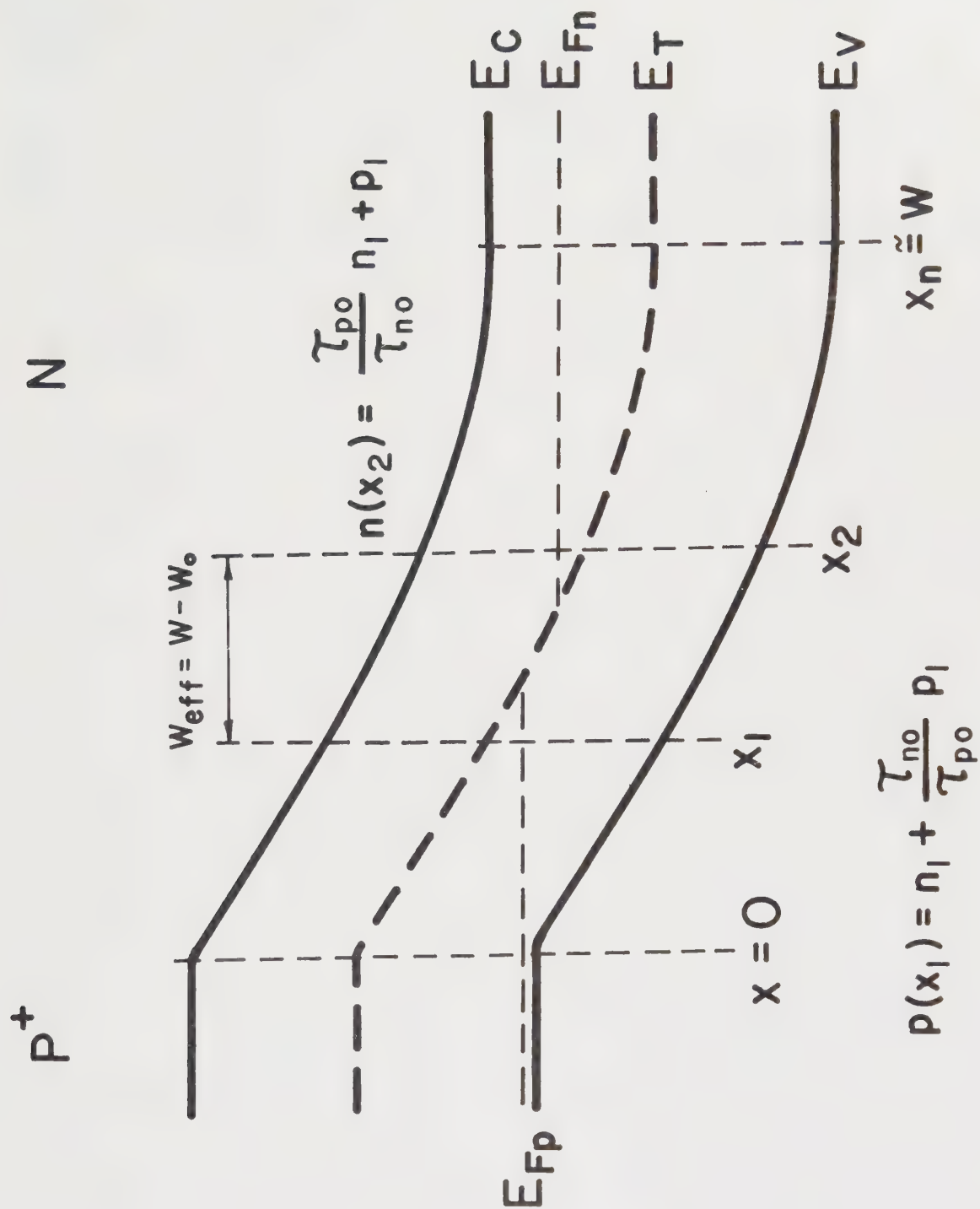
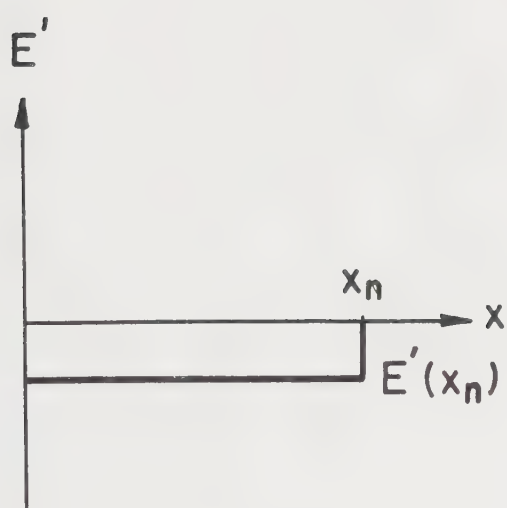
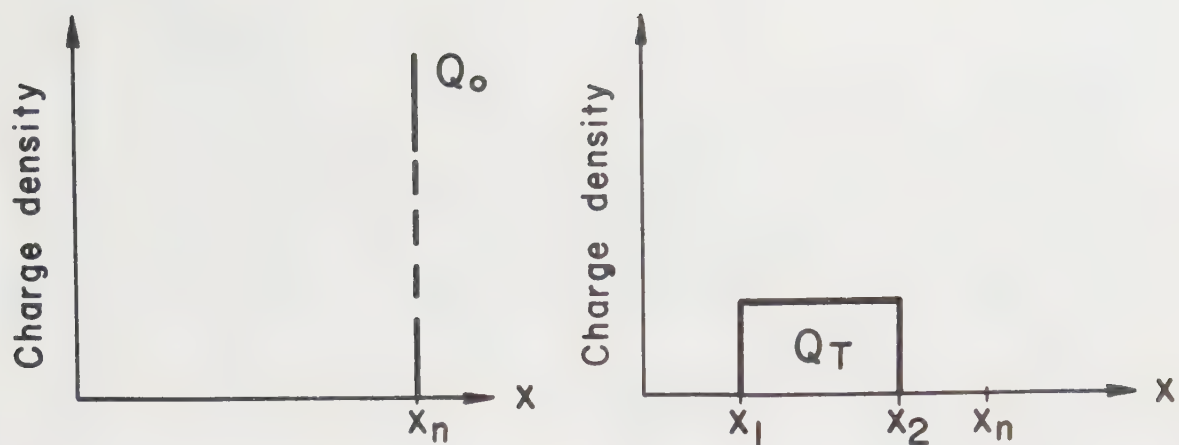
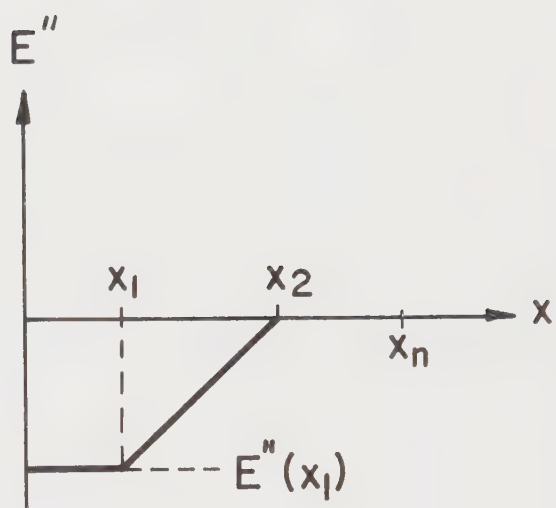


Fig. 1



a)



b)

Fig. 2

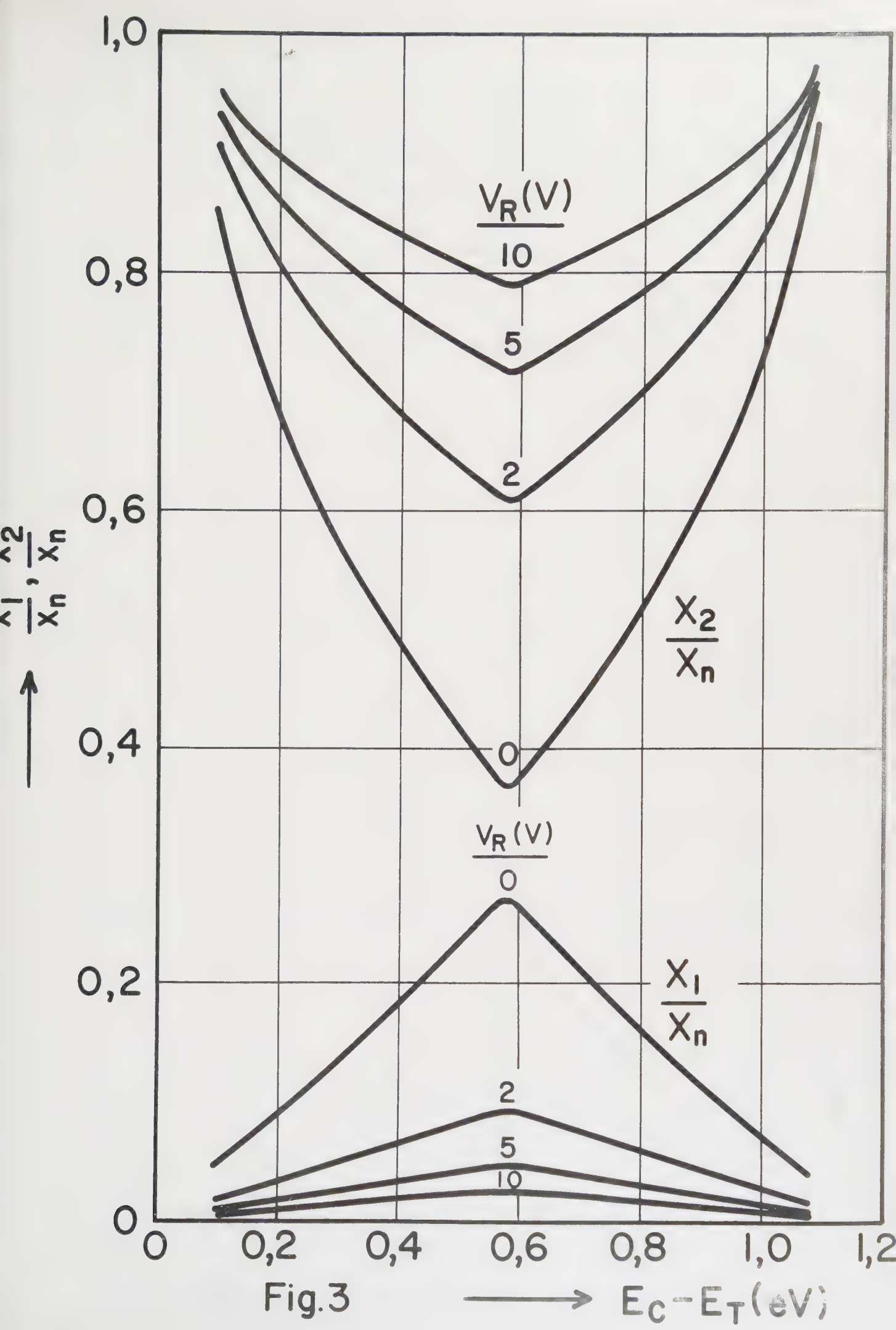


Fig.3

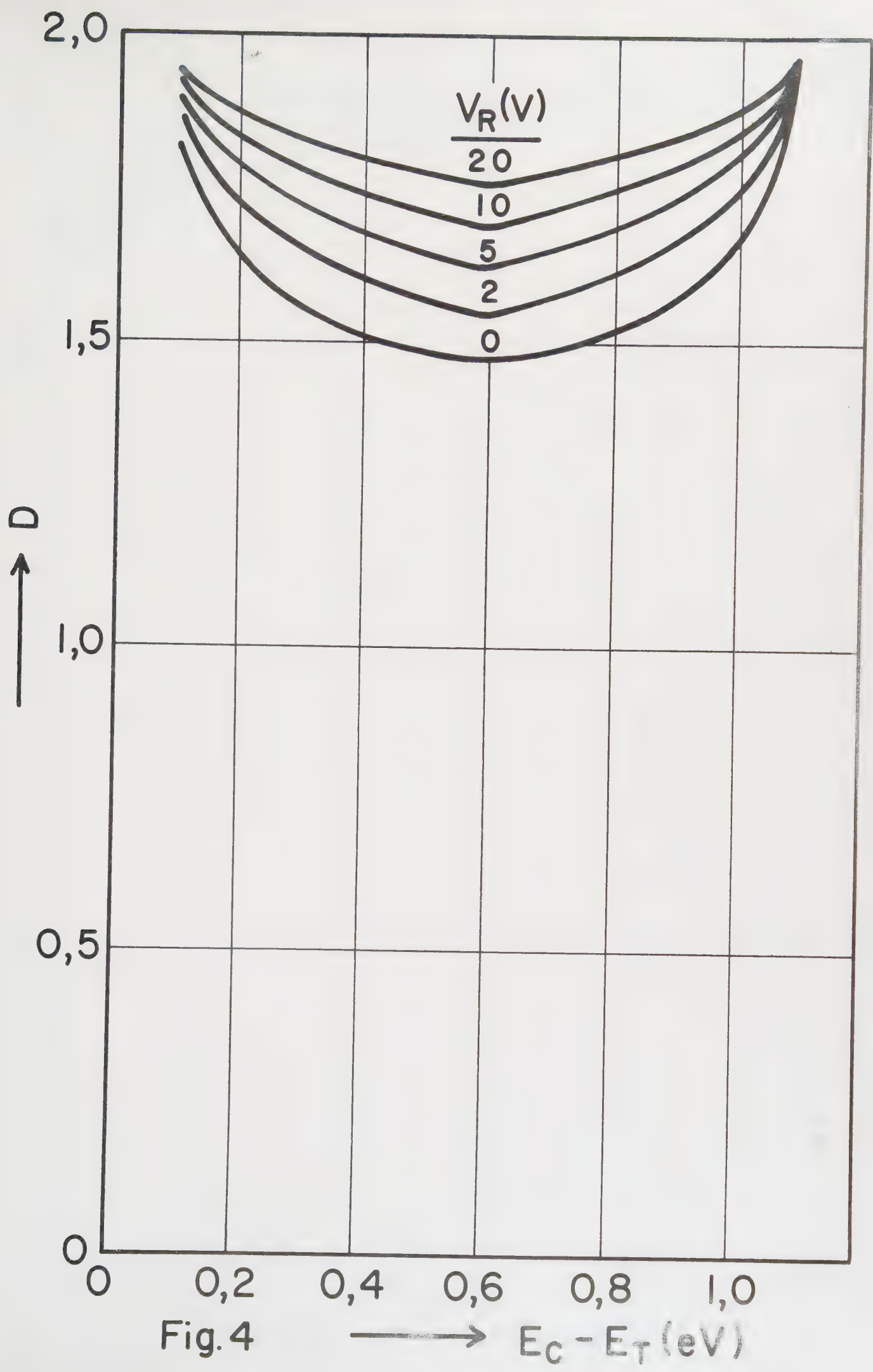


Fig.4

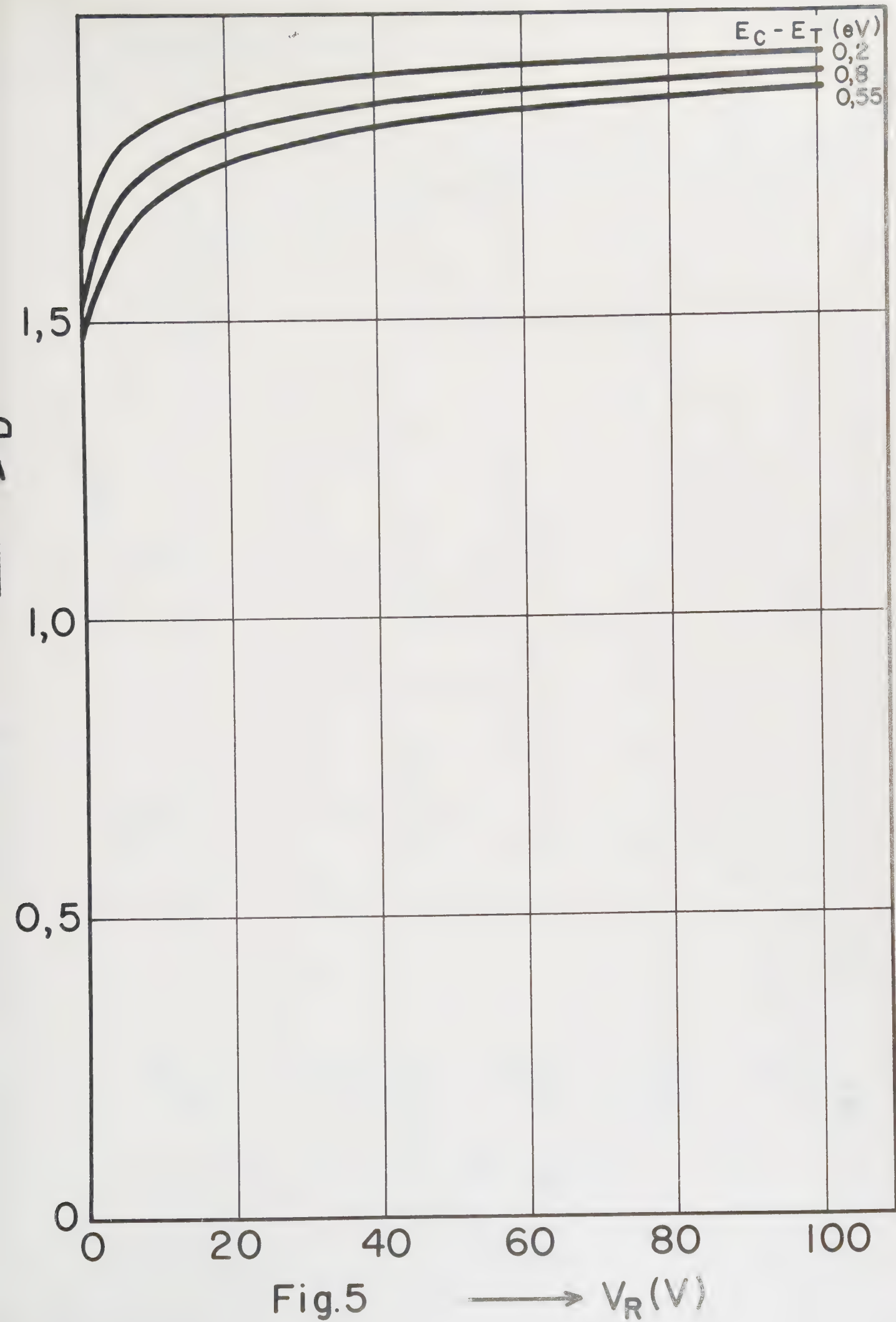


Fig.5

→ V_R (V)

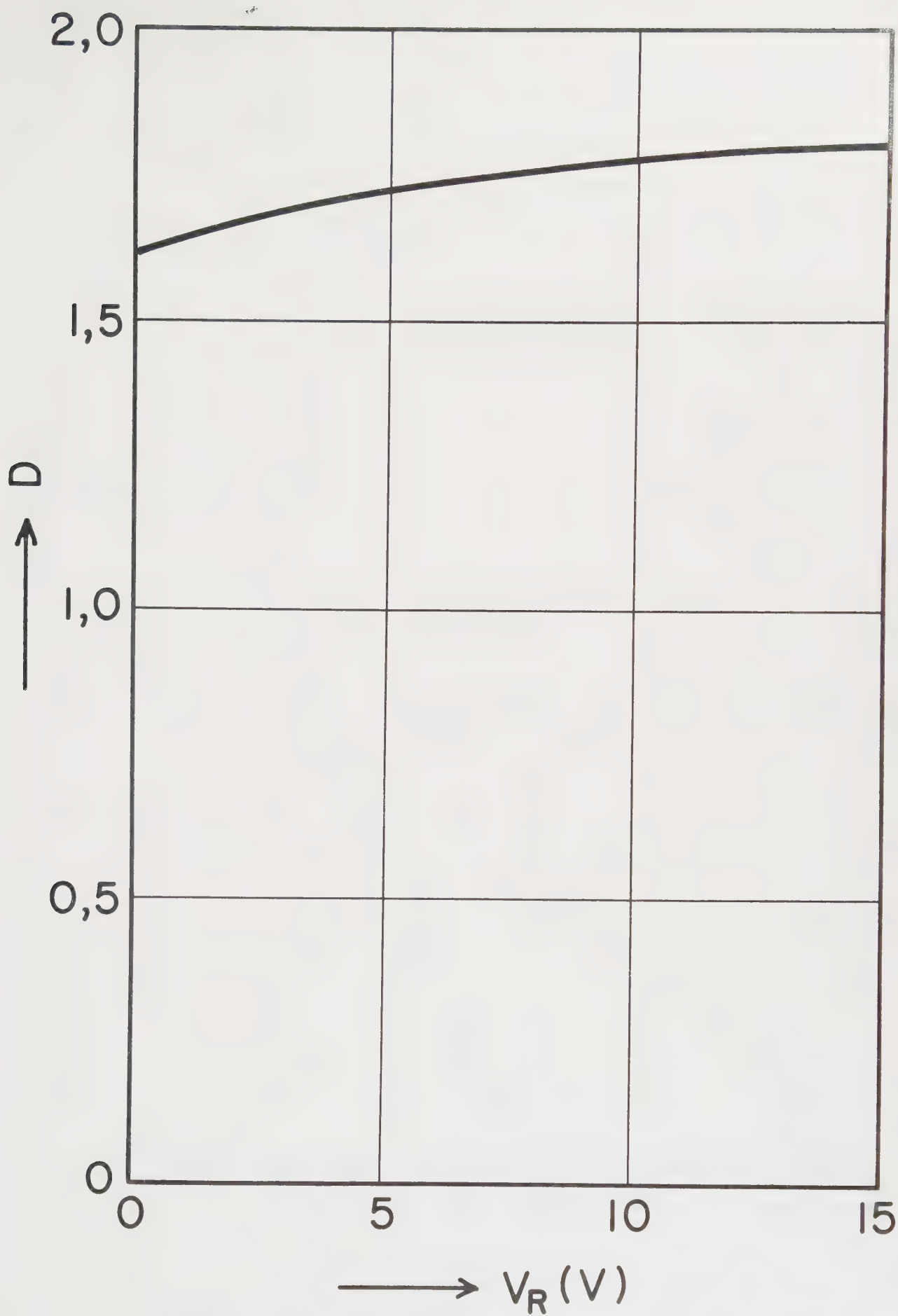


Fig. 6

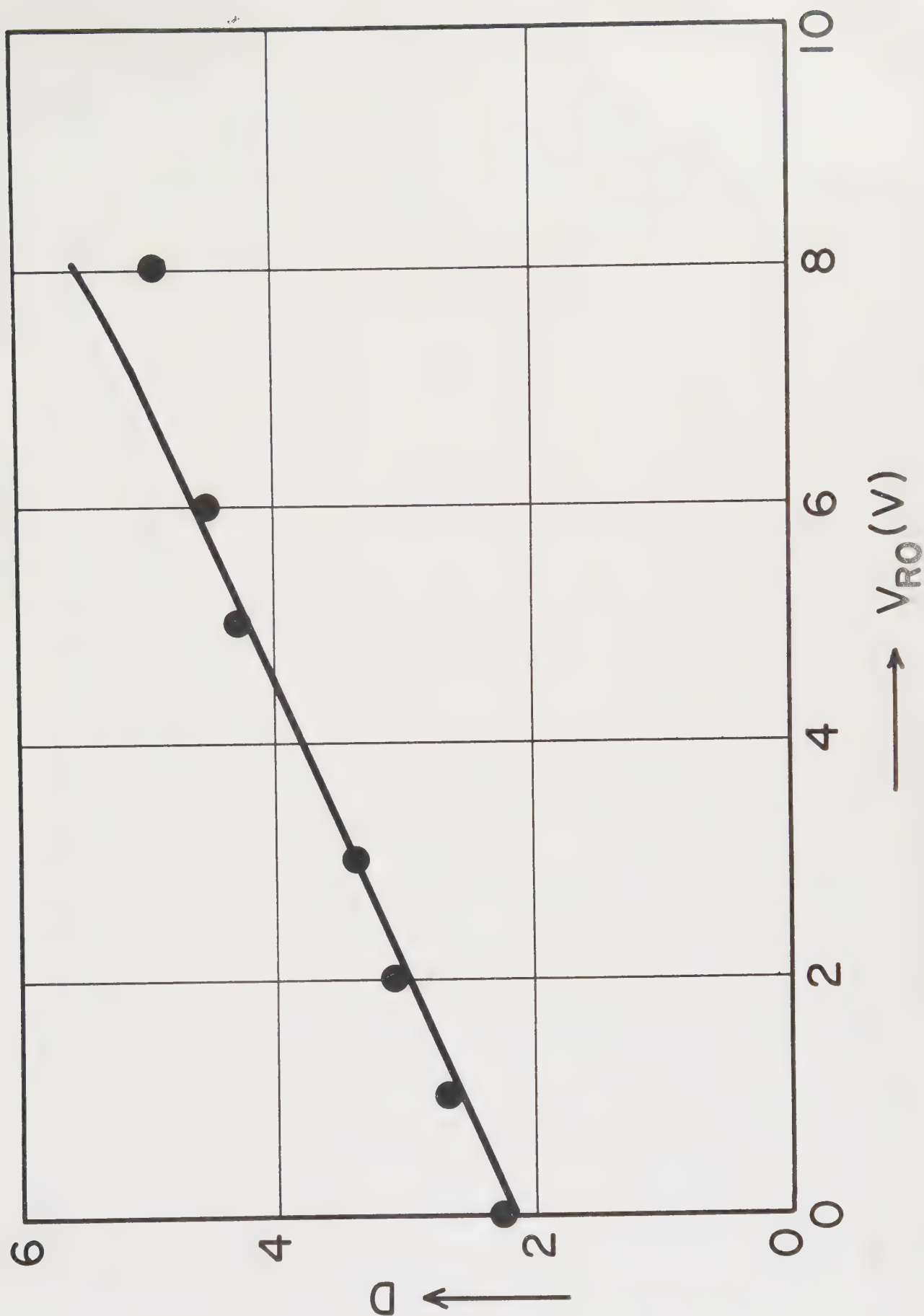


Fig. 7

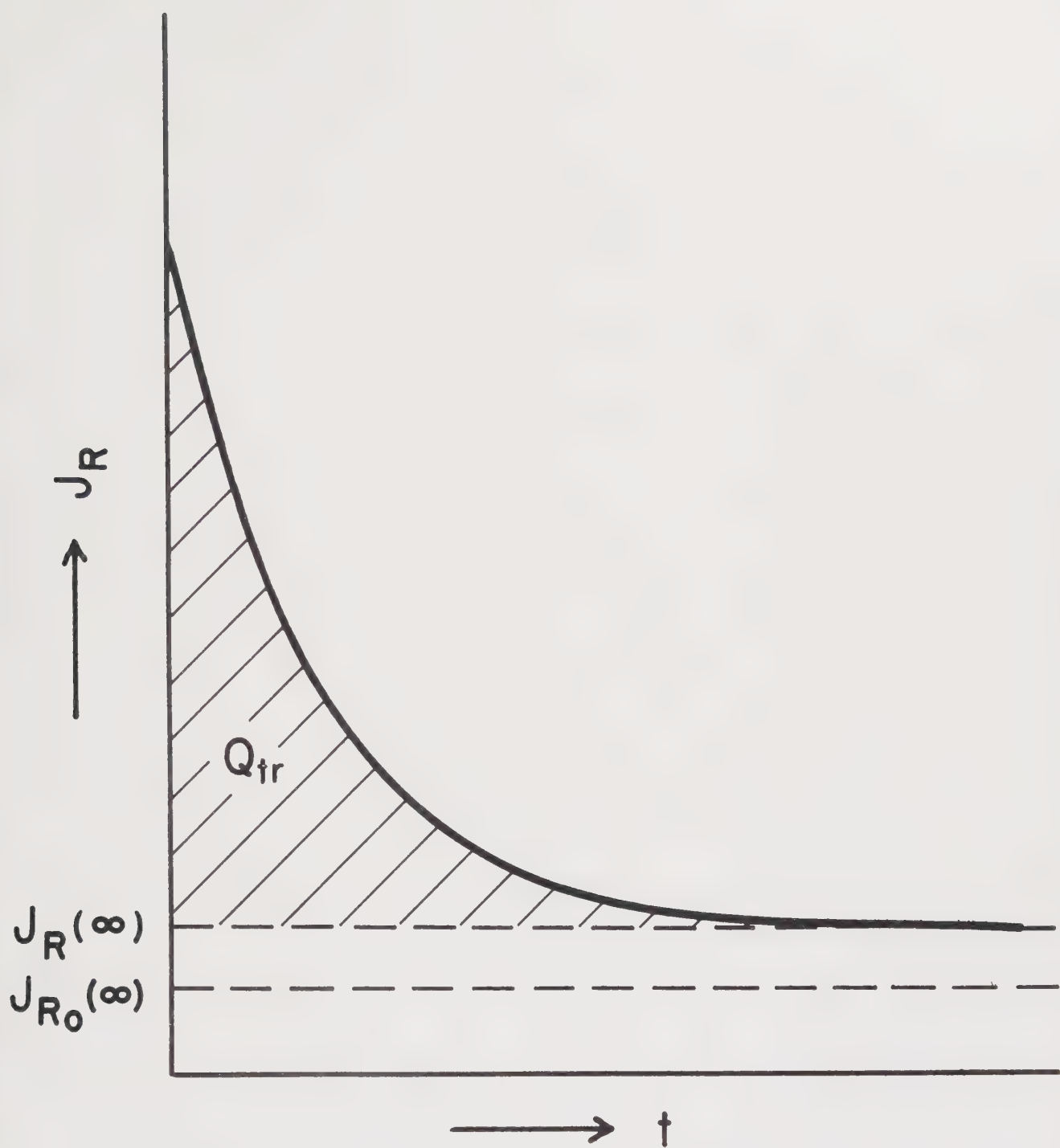


Fig. 8

Optical properties of sulfur doped silicon

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Abstract

Photocurrent measurements in sulfur doped silicon PN-junctions have been used to determine optical threshold energies, ground state energies and spectral distributions of the photoionization cross sections associated with two deep sulfur centers in silicon. It is shown that Coulombic perturbation potentials for electrons in the two centers are in accordance with the experimentally observed cross section spectra and ground state energy levels. However, for holes captured in the deepest sulfur level a delta-function potential gives a better description of the photoionization cross section spectrum. The sum of the ground state energies for electrons and the optical threshold energies for holes exceeds the band gap energy value of silicon.

Optical properties of sulfur doped silicon

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1. Introduction

Photoionization is one of the most widely used techniques for investigations of deep bound electron and hole states in semiconductors^{1,2)}. This technique not only provides accurate values for threshold energies but can give information on the strength of electron lattice coupling and perturbation potentials. The energy positions of shallow impurities in silicon and germanium arising from group III and V elements are rather well described by the so called Kohn-Luttinger Effective Mass Theory (KL-EMT)^{3,4)}. In this treatment, the impurity potential is assumed to arise from a point charge screened by the lattice giving a hydrogenic spectrum of energy levels. This approach has given results in excellent agreement with experiments for the excited states of shallow centers. For the ground state of shallow centers and for deep centers, however, the Coulomb potential can not be used because faster varying contributions to the potential appear in the impurity core region. Recently the KL-EMT has been reformulated using first principle impurity potentials⁵⁾. It has been shown that the KL-EMT is valid for both shallow and deep levels but only if the impurity is substitutional and isocoric. For silicon, this means that phosphorus and sulfur can be described by KL-EMT. The

potentials of these two impurities were found to be nearly equal to the bare Coulomb potential of one or two point charges respectively ⁵⁾.

It has been shown experimentally that for deep centers a delta-function approach is in many cases in accordance with the spectral distributions of photoionization cross sections^{2,6-10)}. For sulfur, therefore, the spectral distribution of the photoionization cross section would be expected to be different from those of other deep impurities with narrower potentials.

Furthermore, for donors for which the KL-EMT is applicable, the wave functions of captured electrons can be expanded in terms of Bloch-functions for electrons in the conduction band. This implies that donor energy levels would be pinned to the conduction band and correspondingly that acceptor energy levels would be pinned to the valence band when the temperature is changed. For deep acceptor centers of cobalt and gold in silicon for which narrow impurity potentials are to be expected, it has been found that the energy levels are fixed to the conduction band^{11,12)}. Because substitutional sulfur can be described by EMT and introduces deep energy levels in silicon, it would therefore (as the only exception) behave very differently from other deep level impurities. This makes sulfur doped silicon particularly interesting to study.

Although the physical properties of sulfur in silicon have been studied extensively, there still exists considerable disagreement in the published values of energy positions of sulfur levels. Using infrared absorption spectra, Krag et al observed four energy levels which they denoted A,B,C and D with ground state energies of 0.109 eV, 0.187 eV,

0.368 eV and 0.612 eV below the conduction band¹³⁻¹⁵⁾. As demonstrated in table I, although the values of ground states obtained by other authors are different from these data they can rather well be classified into these four groups. An exception is the measurement of the thermal emission rates by Rosier and Sah¹⁹⁾ which gives thermal activation energies of 0.276 eV and 0.530 eV. These values, however, were obtained without taking into account possible temperature dependences of the capture rates and energy position of the levels²⁴⁾. The same authors also measured photoionization cross sections for the excitation of electrons from two of the sulfur centers to the conduction band from which the optical threshold energy of one of the transitions was deduced²⁰⁾. In addition, structures in the photoionization cross section spectra below the extrinsic edge of the deepest sulfur donor were attributed to two step photothermal excitation processes via excited states of the center. It has been suggested¹⁸⁾ that the A and C levels might belong to the same double donor impurity coming from a pair of sulfur atoms and that the B and D levels might arise from a double donor level due to an isolated sulfur atom. No published values for optical threshold energies between the sulfur levels and the valence band are available. Also, to the best of our knowledge, no optical cross section spectra for the excitation of electrons from the valence band into the sulfur levels have been published. There is no information available about the temperature dependence of the energy position for the D-level.

The purpose of this paper is therefore to present for the first time all four optical threshold energies connected with the C- and D- centers together with spectral distributions of optical ionization cross sections. It will be shown that these experimental results are consistent

with the Pantelides-Sah correction of KL-EMT. Furthermore, it will be shown that structure observed in the photoionization cross section spectra³¹⁾ is still observed for energies above the ground state energy and may be explained by phonon assisted transitions. Finally, evidence will be given that the D-level is mainly pinned to the conduction band when temperature is changed.

2. Photoionization cross sections

The probability for optical transitions from an impurity energy level to a band state is given by the Fermi Golden Rule as

$$\dot{P} = \frac{2\pi}{\hbar} \left| \langle f | \hat{H} | i \rangle \right|^2 \rho(E) \quad (1)$$

where $\rho(E)$ is the density of states in the band and $\hat{H}$ is the perturbation operator

$$\hat{H} = - \frac{q}{m} \hat{p} \bar{A} \quad (2)$$

$\bar{A}$ is the vector potential of the radiation field, $\hat{p}$ is the momentum operator, m is the electron mass and q is the electron charge.

For transitions to the conduction band, we assume that the density of states function $\rho(E)$ is determined by bands with ellipsoidal energy surfaces and paraboloidical energy dependence in k -space. The density of final states is then given by

$$\rho(E) = \frac{4\pi\sqrt{2}}{h^3} m^{*3/2} (\hbar\nu - E_i)^{1/2} \quad (3)$$

where $E_i = E_c - E_T$ is the optical threshold energy and m^* is the averaged density of states mass for electrons in silicon.

Earlier investigations on sulfur doped silicon¹³⁻¹⁵⁾ have shown that excited states are present at all four sulfur centers. This together with the theoretical investigations in ref 5 indicates that the electrons are captured by a very broad potential. According to ref 5, we therefore use for the initial state ψ_i in the matrix element of eqn (1) a 1s hydrogen wave function. Following further the intentions of Anderson²⁵⁾, ie, taking into account spin selection in the excitation process and using Bloch waves for the final states ψ_f , we find for the photoionization cross section σ_n^0

$$\sigma_n^0 = \left(\frac{\epsilon_{\text{eff}}}{\epsilon_0} \right)^2 \gamma \frac{32}{3} \frac{q^2 \hbar E_i^3}{n c m^*} \frac{(h\nu - E_i)^{3/2}}{(h\nu)^5} \quad (4)$$

where n is the refractive index of silicon and c is the velocity of light in free space. In eqn (4) a correction has further been made due to the possibility of a localized wavefunction by introducing the effective field ratio $\epsilon_{\text{eff}}/\epsilon_0$ ²⁶⁾. Another correction is the factor γ which takes a value not equal to 1 if a many electron configuration is excited.

As soon as the electron is excited to the conduction band, the isolated sulfur atom is doubly ionized. From this follows that a hole, after being excited to the valence band, will meet a repelling Coulomb potential at long distances from the center and a narrow attracting core potential in the central cell region (fig 1). Such a picture is experimentally supported by the measurements of Lebedev et al²²⁾.

Assuming that the excitation of a hole to the valence band can be treated in the same formalism as the excitation of an electron to the conduction band we use in eq (1) a wave function for the bound hole which is determined by a delta-function potential⁶⁾. Furthermore, for transitions to the valence band, the rather complicated structure of the latter has to be taken into account. In ref 7, the valence band structure was calculated from data which were obtained with gold doped silicon. For the theoretical photoionization cross section of holes from the doubly ionized sulfur donor into the conduction band we therefore used the results of ref 7.

3. Experimental details

All experiments were performed on sulfur doped P⁺N-junctions prepared by diffusion of boron into lightly doped silicon substrates. The samples were sulfur diffused in the temperature range between 1050C and 1200C during 20 h in evacuated quartz ampoules of suprasil quality giving a sulfur impurity concentration between $1.5 \cdot 10^{13} \text{ cm}^{-3}$ and $1.3 \cdot 10^{14} \text{ cm}^{-3}$. Sulfur is known to react with silicon at high temperatures causing erosion and mass transport¹⁶⁾. This has been avoided in our case by mixing the sulfur with pulverized silicon during the diffusion process²⁷⁾. Control diodes were made by passing samples through the same temperature cycle as during the sulfur diffusion. Typical junction photocurrent spectra for a sulfur doped sample and a control sample are shown in fig 2.

Spectral distributions were measured using a Zeiss MM12 double prism monochromator and two tandem coupled 0.25 m Jarrel Ash grating mono-

chromators with 5μ , 2μ and 1μ interchangeable gratings. Currents were measured with a Keithley 602C electrometer in conjunction with a Goerz strip chart recorder and a Keithley 427 current amplifier connected with a Nicolet transient recorder. All optical measurements were made below the "freeze out" temperature for trapped carriers. The lowest temperature used was 77K and the cooling unit was an Oxford Instruments Cryostat DN704 with sapphire windows. In order to avoid stray light Ge- and Si-filters were used for measurements performed in the extrinsic energy range. The monochromators were calibrated with a thermocouple and the absolute calibration was made with a pyroelectric detector from Laser Corporation, model Rk 3240.

For energies above 250 meV, only two centers caused by the sulfur diffusion could be identified in our samples.

4. Measuring procedure and experimental results

Optical emission rates were measured using the photocurrent transient technique¹⁾. The technique involved the measurement of decay time constant and the initial and final photocurrents $J_R^0(0)$ and $J_R^0(\infty)$ respectively, when the junction was illuminated with photons of energy $h\nu$. It has been shown^{1,28)} that the optical emission rates for electrons and holes e_n^0 and e_p^0 , respectively, can be calculated from the transient wave forms according to the following expression:

$$e_n^0 + e_p^0 = \tau^{-1} \quad (5)$$

$$\frac{e_n^0}{e_p^0} = D \frac{J_R^0(0)}{J_R^0(\infty)} - 1 \quad (6)$$

where the steady state photocurrent is given by

$$J_R^0(\infty) = qA(W-W_0)N_{TT} \frac{e_n^0 e_p^0}{e_n^0 + e_p^0} \quad (7)$$

It should be noted that the factor D depends on the experimental conditions and can in principle take any value larger than 1. In a separate paper, a measurement technique is presented by which D -factors can be determined²⁸⁾. Under the experimental conditions used in this paper, this factor for the deepest sulfur level has a value close to 2.

The two centers found exhibited optical thresholds at about 0.3 eV and 0.55 eV from the conduction band respectively. It will be shown that the two thresholds correspond to ground state energies of 0.37 eV and 0.61 eV in accordance with the C- and D-levels in table 1. When transient measurements were performed below 0.55 eV, $J_R^0(\infty)$ was zero. In this energy range, the current transient is determined by the emission of electrons from the C-level and from eqns (5) and (6) it can be seen that the emission rate for electrons at the C-level is then given by $e_{nC}^0 = 1/\tau$. The D-level was investigated by first emptying the C-level with a photon energy of about 0.4 eV. After that, the measurements on the D-level were made in the region 0.53 - 1.1 eV. For energies smaller than about 0.65 eV, it was found that $J_R^0(\infty) \ll J_R^0(0)$. In this region therefore the emission rate for electrons from the D-level is given by $e_{nD}^0 \cong 1/\tau$ and the emission rate for holes e_{pD}^0 is proportional to $J_R^0(\infty)$ as can be seen from eqn (7). For higher energies, however, $J_R^0(\infty)$ becomes of the same order as $J_R^0(0)$ and a typical current transient

for this case is shown in fig 3.

From the optical emission rates, the absolute values of the photoionization cross sections σ^0 are obtained by the relation

$$\sigma^0 = \frac{e^0}{\phi} \quad (8)$$

where ϕ is the photon flux used for measuring e^0 . Fig 4 shows the spectral distributions of σ_{nC}^0 , σ_{nD}^0 and σ_{pD}^0 in absolute values.

Determination of the optical emission rates of holes e_{pC}^0 due to the excitation of electrons from the valence band into the C-level could not be done rigorously although the optical threshold energy was found by the following procedure. First, the sample was illuminated with photons of energy $h\nu$ large enough to achieve a two step excitation via the C-level (fig 5a). After steady state had been reached, the light source was removed, the C-level was emptied with photons of energy 0.4 eV (fig 5b) and the charge ΔQ_C passing the outer circuit as a result of this procedure was measured. Values of e_{pC}^0 can then be calculated if e_{nC}^0 is known. Two cases must be considered depending on whether or not the two levels are coupled. Ludwig has concluded from paramagnetic resonance studies²⁹⁾ that the D-level belongs to an isolated sulfur atom while the C-levels belongs to a sulfur pair. The two centers have different symmetry properties and it might be concluded that the C- and D-levels are not coupled. It has, however also been observed³⁰⁾ that the two centers appear at the same concentration (which was also found in the present work), indicating that the C- and D-levels are coupled.

If the levels are not coupled, the charge ΔQ_C can be expressed as ²⁸⁾

$$\Delta Q_C = B b_C N_{TTC} \quad (9)$$

where B is a constant involving the effective space charge region, the D-factor and the electron charge, N_{TTC} is the concentration of C-centers and

$$b_C = \frac{n_{TC}}{N_{TTC}} \quad (10)$$

is the electron occupancy factor. The total charge Q_C measured in the outer circuit when the C-level is completely filled is given by

$$Q_C = B N_{TTC} \quad (11)$$

Because recombination in the effective space charge region can be neglected we have at steady state

$$e_{nC}^0 n_{TC} = e_{pC}^0 (N_{TTC} - n_{TC}) \quad (12)$$

Using eqns (9) - (12), e_{pC}^0 can be expressed in this case as

$$e_{pC}^0 = \frac{e_{nC}^0}{\frac{Q_C}{\Delta Q_C} - 1} \quad (13)$$

If the C- and D-levels are coupled, the situation is somewhat more complicated. The first electron captured then belongs to the D-level. When the center captures the second electron, both belong to the C-level because of the indistinguishability of the particles. The concentration of centers N_{TT} is then given by

$$N_{TT} = p_{TD} + n_{TD} + n_{TC} \quad (14)$$

where p_{TD} , n_{TD} and n_{TC} are the concentrations of centers occupied by two holes, one electron and two electrons respectively. At steady state, we have in analogy with eqn (12)

$$e_{pD}^0 p_{TD} = e_{nD}^0 n_{TD} \quad (15)$$

$$e_{pC}^0 n_{TD} = e_{nC}^0 n_{TC} \quad (16)$$

Using eqns (14) - (16) and considering that ΔQ_C is now $\Delta Q_C = Bb_C N_{TT}$ and $Q_C = BN_{TT}$, e_{pC}^0 can be expressed as

$$e_{pC}^0 = \frac{e_{nC}^0}{\frac{e_{pD}^0}{e_{nD}^0 + e_{pD}^0} \left(\frac{Q_C}{\Delta Q_C} - 1 \right)} \quad (17)$$

Comparing eqn (13) and (17), one finds that e_{pC}^0 varies by a factor $e_{pD}^0 / (e_{nD}^0 + e_{pD}^0)$ depending on whether or not the two levels are coupled. Because we have no detailed information about e_{nC}^0 in the energy region 0.8-1.1 eV where e_{pC}^0 was measured, the absolute values of e_{pC}^0 cannot be calculated properly. It should however be noticed that ΔQ_C approaches zero at the threshold energy of e_{pC}^0 and that therefore a plot of ΔQ_C versus photon energy gives information about the optical threshold energy for holes from the C-level to the valence band. ΔQ_C as a function of photon energy is shown in fig 6.

5. Optical threshold energies of the C-center

The spectrum of σ_{nC}^0 clearly shows an optical threshold energy at about 0.3 eV (fig 4). Krag et al¹³⁻¹⁵⁾ have found that all four sulfur centers have excited states. This may imply that the electrons in the C-centers are captured by a broad potential and that eqn (4) is valid in the case of excitation from the C-level. Eqn (4) can be rewritten in the following way

$$\left[\sigma_n^0 (h\nu)^5 \right]^{2/3} = \text{const.} (h\nu - E_i) \quad (18)$$

Hence by plotting $[\sigma_n^0 (h\nu)^5]^{2/3}$ versus the photon energy, a straight line intercepting the energy axis at E_i is expected. However, fig 7 shows a curve on which two interceptions are observed, one at about 0.29 eV and another at 0.37 eV. The value of 0.37 eV is in good agreement with published values¹⁴⁾ of the ground state energy of the C-center. The 0.29 eV threshold energy might therefore be due to photothermal excitation via an excited state 0.08 eV below the conduction band edge.

From the spectral distribution of ΔQ_C (fig 6) the optical threshold energy of e_{pC}^0 is found at about 0.81 eV. No signal has been found for energies 0.81 eV and smaller. The sum of the ground state energy for electrons and the threshold energy for holes $0.37 + 0.81 = 1.18$ eV exceeds the band gap energy of silicon at 100K by about 15 meV.

6. Optical threshold energies for the D-center

From what has been said in section 2, it is expected that the photoionization cross section for electrons from the D-level into the conduction band is described by eqn (4). Using eqn (18) and plotting $[\sigma_n^0 (h\nu)^5]^{2/3}$ versus photon energy should give a straight line with an intercept on the energy axis at E_i . Figure 8, however, shows that a more complicated curve is obtained. In the lower energy region, a linear part is observed from which a threshold energy of about 0.55 eV is deduced. At higher energies, another linear part is observed. Extrapolation of this part gives an intercept on the energy axis at about 0.61 eV (fig 8, dotted line). This energy which is observed at both 80K and 160K is close to the ground state energy of the D-level as measured by Krag et al¹⁴⁾. Hence, using $E_i = 0.61$ eV and plotting the logarithm of σ_{nD}^0 as calculated from eqn (4) versus photon energy, agreement with measured data is observed only for energies larger than about 0.7 eV (fig 9). In fig 9 also the calculated cross section from eqn (4) using $E_i = 0.55$ eV and a cross section based on a delta-function potential and $E_i = 0.61$ eV are shown. In the latter case no agreement with the experimental data is obtained.

It has already been mentioned in section 2 that optical ionization cross sections for holes from the D-level into the valence band are probably better described by a delta-function potential. In fig 10 measured σ_{pD}^0 -values are compared with photoionization cross sections which have been calculated for both a Coulomb potential and for a delta-function potential⁷⁾ using an optical threshold energy of 0.570 eV. It is clearly

seen that a narrow impurity potential gives a better agreement than does a Coulombic one.

The spectrum of σ_{nD}^0 was measured with higher resolution in the energy region 0.53 - 0.7 eV. In fig 11 where a linear plot of σ_{nD}^0 is shown, a pronounced structure is observed with thresholds at 0.547, 0.564, 0.578, 0.598, 0.628, 0.655 and 0.679 eV. This structure has previously been reported for the energy region below 0.61 eV and was interpreted as photothermal excitation via excited states of the D-center³¹⁾. In fig 11, three humps with maximum points starting at 0.578, 0.598 and 0.655 eV respectively can be seen. Considering that the ground state is at 0.61 eV, the hump with a threshold at 0.578 eV might be interpreted as an excited state³¹⁾ and the two thresholds at 0.598 eV and 0.655 eV as phonon replica by emission of a TA-phonon and a TA- plus an optical phonon.

A structure is also found for σ_{pD}^0 giving four different thresholds labeled E_1 , E_2 , E_3 and E_4 in fig 12. This measurement was made at different temperatures in the region 77 - 182K and the four thresholds are listed in table II. As can be seen, the threshold energies E_1 , E_2 and E_3 are temperature dependent while E_4 is independent of temperature. The thresholds E_1 , E_2 and E_3 can be interpreted as results of phonon interaction. The value E_4 coincides with one of the thresholds in σ_{nD}^0 at 0.628 eV. The measurement of σ_{pD} in fig 12 was however made by measuring the steady state photocurrent $J_R^0(\infty)$. In the energy region where σ_{pD}^0 has been measured it is seen from fig 4 that the electron occupancy factor increases strongly reaching a level of some percent in the region at about 0.63 eV. A change in σ_{nD}^0 would therefore be

seen as a small change in $J_R^0(\infty)$. The threshold at E_4 obviously originates from the structure of σ_{nD}^0 , again indicating that the sulfur D-levels are mainly fixed to the conduction band.

7. Temperature dependence of spectral distributions for the D-level

In fig 8 the spectral distribution of σ_{nD}^0 is shown at 80K and 160K. No pronounced temperature dependence is observed. Spectra of $\log \sigma_{pD}^0$ at five different temperatures are shown in fig 13. The curves are normalized to the 77K-data in order to demonstrate that the curve form remains the same for all temperatures. This was achieved by shifting the curves to higher energies by 2 meV at 101K, 10 meV at 135K, 25 meV at 191K and 36 meV at 223K thus showing that $E_T - E_V$ is temperature dependent. In fig 10 it was found by comparison of σ_{pD}^0 with theory that the optical threshold is 0.570 eV at 100K. Looking at table II, one finds that at 101K the thresholds E_1 , E_2 and E_3 are 17 meV, 27 meV and 40 meV larger than this value respectively. In table III, the energies of 17 meV, 27 meV and 40 meV have been subtracted from the threshold energies E_1 , E_2 and E_3 for all temperatures. It can be seen that the three thresholds have similar temperature dependence. Taking the ground state energy position for electrons, $E_C - E_T$, from ref 14 (0.612 eV) as temperature independent and adding this value to the energies in table III, an energy sum comparable with the energy band gap of silicon should be obtained. Such a comparison has been made in fig 14 where the band gap values at different temperatures have been taken from the investigation by Bludau et al³²⁾. In fig 14 the sum of 0.612 eV and the energy thresholds found in fig 13 is also plotted. As can be seen, the sums of ground state energy for electrons and threshold energy for

holes at all temperatures exceed the band gap value of silicon and have a similar but slightly larger temperature dependence.

When σ_{nD}^0 was measured at 160K a hump was found at about 0.47 eV (fig 15). This behaviour was observed previously^{20,31)} and has been explained as a photothermal excitation via an excited state of the D-level.

8. Discussion

The cross section for the optical excitation of electrons from the D-level to the conduction band was previously investigated by Rosier and Sah²⁰⁾. They found good agreement between the theoretical cross section based on a delta-function potential and experiment in the energy region above 0.7 eV. This is in contradiction to our results (fig 9). Their calculation of σ_{nD}^0 was however made using the expression $e_{nD}^0 = 1/\tau$, where τ is the time constant defined in eqn (5), in the energy region where this approximation no longer holds. As can be seen in fig 4, above 0.7 eV σ_{pD}^0 becomes of the same order as σ_{nD}^0 . The result of the measurement in ref 20 is therefore not σ_{nD}^0 but $\sigma_{nD}^0 + \sigma_{pD}^0$.

The absolute value of σ_{pC}^0 could not be determined in this work. However, looking at fig 6, it is readily seen that if σ_{pC}^0 were of the same order as σ_{pD}^0 , the structure of the former would very dramatically influence the measurement of σ_{pD}^0 . Because no pronounced structure has been found in this energy region, we conclude that $\sigma_{pC}^0 \ll \sigma_{pD}^0$.

Summing the ground state energy for electrons and the optical threshold energy for holes, it is found that for both the C- and the D-center an

energy is obtained which is larger than the band gap value of silicon by an amount of about 15 meV at 100K. This might be explained by the vibrational properties of the sulfur impurity. When an electron is excited from the valence band into the center or from the center to the conduction band, a lattice relaxation might occur due to the sudden change of charge in the vicinity of the impurity. This would give rise to a static change in the vibrational coupling between the impurity and the silicon lattice and the energy difference would be that due to a Frank-Condon shift²⁶⁾. The structure found in σ_{nD}^0 - and σ_{pD}^0 -distributions (fig 11 and 12) can be explained in this picture as interaction with local phonons. This is in accordance with the near equidistance between E_1 , E_2 and E_3 in fig 12 and table III.

The energy difference found, however, also is one of a number of parameters in agreement with what is expected on the basis of the potential model in fig 1. These are:

- a) The sum of the ground state energy distance to the conduction band for an electron and the threshold energy distance to the valence band for a hole might be expected to exceed the band gap energy in this potential model. The energy portion exceeding the band gap energy would be interpreted as the potential barrier for holes and the structure in the spectral distributions for σ_{nD}^0 and σ_{pD}^0 (fig 11 and 12) would be due to interaction with momentum-conserving phonons.
- b) The potential for electrons is expected to be broad. This is experimentally confirmed in fig 7,8 and 9. Furthermore

excited states for electrons have been found in this and previous works^{13-15, 20, 30)}.

- c) The potential for holes is expected to be narrow. This is in accordance with comparisons between the theoretical and experimental spectra for σ_{pD}^0 in fig 10.
- d) The capture rate for holes should increase with increasing external electric field. Injection of holes into a sulfur doped silicon crystal should therefore give rise to a voltage controlled negative differential resistance³³⁾. Such a behaviour has been found in ref 22 for P^+-P-P^+ sulfur doped silicon devices.

9. Conclusions

The optical emission properties of two deep sulfur centers in silicon have been investigated using photocurrent measurement techniques applied to sulfur doped P^+N -junctions. This has yielded information about optical threshold energies, ground state energies and spectral distributions of photoionization cross sections connected with the centers. By comparing theoretical distributions of cross sections with experiment, it was found that a broad impurity potential for electrons can be expected. For the deepest center, however, the distribution of the photoionization cross section indicated that the impurity potential for holes is very narrow. The optical threshold energies for electrons were found at 0.29 eV and 0.55 eV respectively for the two centers. The ground state energies for electrons were found at 0.37 eV and 0.61

eV in accordance with investigations based on absorption measurements¹³⁻¹⁵⁾ and the experiments indicate that the deepest sulfur level is pinned mainly to the conduction band when the temperature is changed. Optical thresholds for holes were obtained at 0.81 eV and 0.570 eV respectively. The sum of the optical threshold energy for a hole and the ground state energy for an electron exceeded the band gap energy of silicon. This is in accordance with what might be the behaviour expected of a double donor due to its potential properties. However, an explanation based on a Frank-Condon shift cannot be excluded by the experimental data. All spectral distribution curves exhibited a more or less pronounced structure which was interpreted as photothermal excitation via excited states and interaction with phonons.

Acknowledgements

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Author	$E_C - E_T$ (eV)				Reference
	A	B	C	D	
Carlson et al		0.18	0.37		16
Krag et al		0.1859	0.3655		13
Krag et al	0.1090	0.1872	0.3683	0.6116	14
Kleiner, Krag	0.10953	0.18766	0.37049	0.61355	15
Camphausen et al	0.13	0.18 , 0.20	0.36		17
Camphausen et al	0.105	0.190	0.360		18
Rosier, Sah				0.591	20
Rosier, Sah			0.275	0.530	19
Lebedev et al		0.19	0.37		21, 22
Lebedev et al			0.28-0.38	0.5	23
This paper			0.37	0.61	

TABLE I. Published data on energy positions of sulfur centers in silicon

T (K)	E ₁ (eV)	E ₂ (eV)	E ₃ (eV)	E ₄ (eV)
77	0.592	0.603	0.616	0.626
101	0.587	0.597	0.610	0.627
125	0.579	0.593	0.605	0.628
160	0.574		0.595	0.628
182			0.585	0.627

TABLE II. Thresholds in the spectral distribution of σ_{pD}^0 at different temperatures

T (K)	E ₁ - 0.017 (eV)	E ₂ - 0.027 (eV)	E ₃ - 0.040 (eV)
77	0.575	0.576	0.576
101	0.570	0.570	0.570
125	0.562	0.566	0.565
160	0.557		0.555
182			0.545

TABLE III. Thresholds E₁, E₂ and E₃ in the spectral distribution of σ_{pD}^0 subtracted with 17 meV, 27 meV and 40 meV respectively at different temperatures

Figure captions

- Fig 1 Potential for an electron and a hole at the D-center
- Fig 2 Junction photocurrent spectra for a sulfur doped (o)
and a control diode (x)
- Fig 3 Typical current transient $J_R^0(t)$ in the high energy region
in logarithmic and linear (inserted) scale
- Fig 4 Absolute values of the photoionization cross sections
 σ_{nC}^0 , σ_{nD}^0 and σ_{pD}^0 versus photon energy
- Fig 5 Schematic illustration of measurement method used to
obtain the optical threshold energy for holes in the
C-center (see text)
- Fig 6 The charge ΔQ_C measured in the outer circuit in the
measurement method described in fig 5
- Fig 7 Photoionization cross section σ_{nC}^0 for electrons in the
C-center linearized with respect to a Coulomb impurity
potential
- Fig 8 Photoionization cross section σ_{nD}^0 for electrons in the
D-center linearized with respect to a Coulomb impurity
potential

- Fig 9 Photoionization cross section σ_{nD}^0 for electrons in the D-center compared with theoretical curves for Coulomb potential and delta-function potential
- Fig 10 Photoionization cross section σ_{pD}^0 for holes in the D-center compared with theoretical curves for Coulomb potential and delta-function potential
- Fig 11 Photoionization cross section for electrons in the D-center in linear scale
- Fig 12 Photoionization cross section for holes in the D-center in linear scale
- Fig 13 Photoionization cross section σ_{pD}^0 for holes in the D-center at different temperatures. The energy scale for the values taken at temperatures above 77K have been shifted to higher energies by the amounts shown in the table inserted.
- Fig 14 Sums of ground state energy 0.612 eV for electrons in the D-center and the threshold energies for holes taken from table III and fig 13 at different temperatures compared with the band gap energy of silicon ³²).
- Fig 15 Photoionization cross section σ_{nD}^0 for electrons in the D-center at 160 K

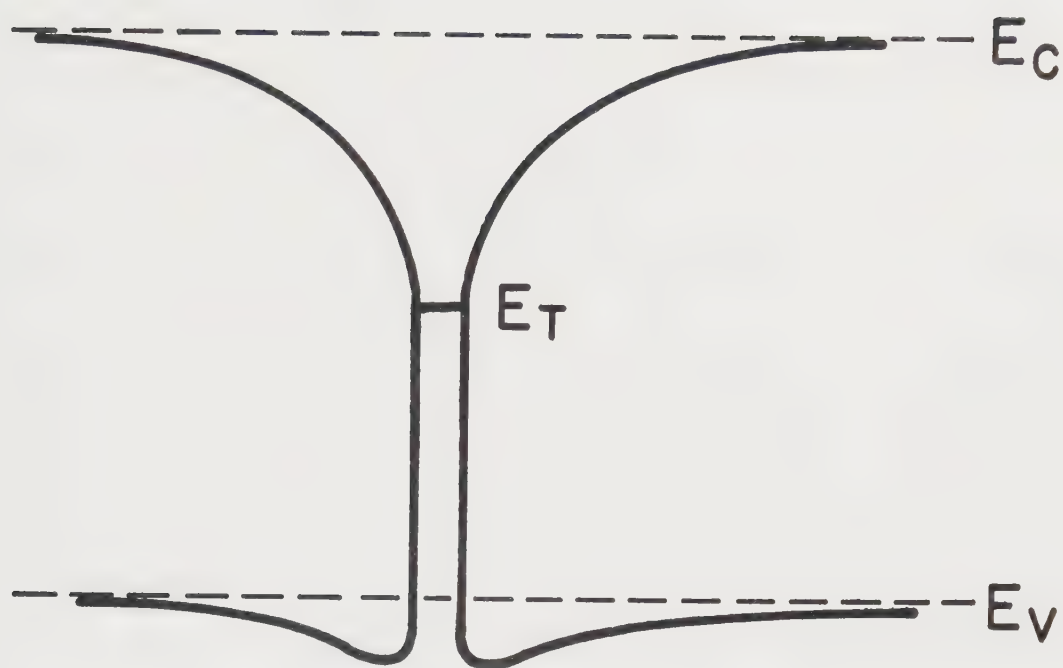


Fig.1

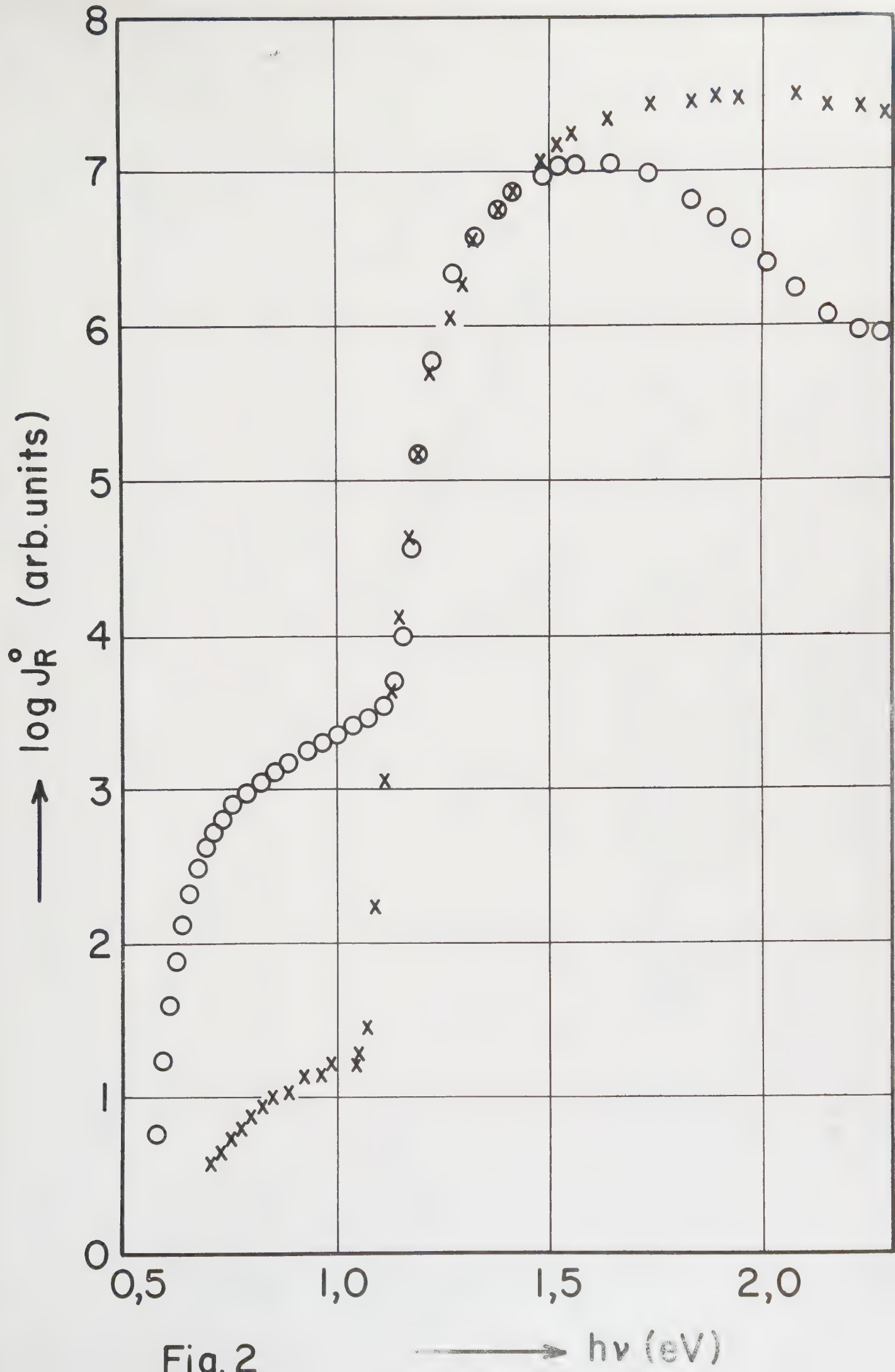


Fig. 2

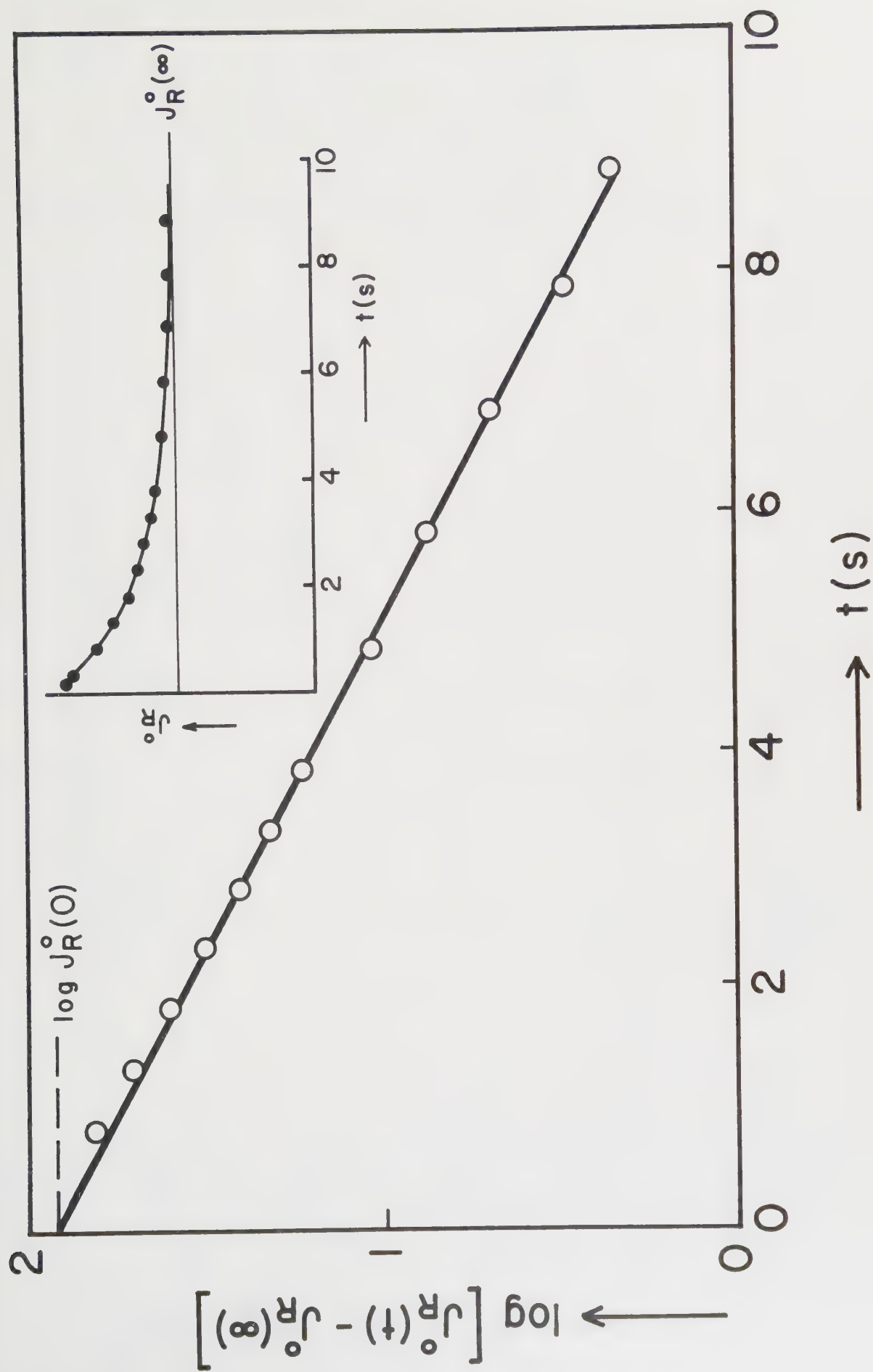


Fig.3

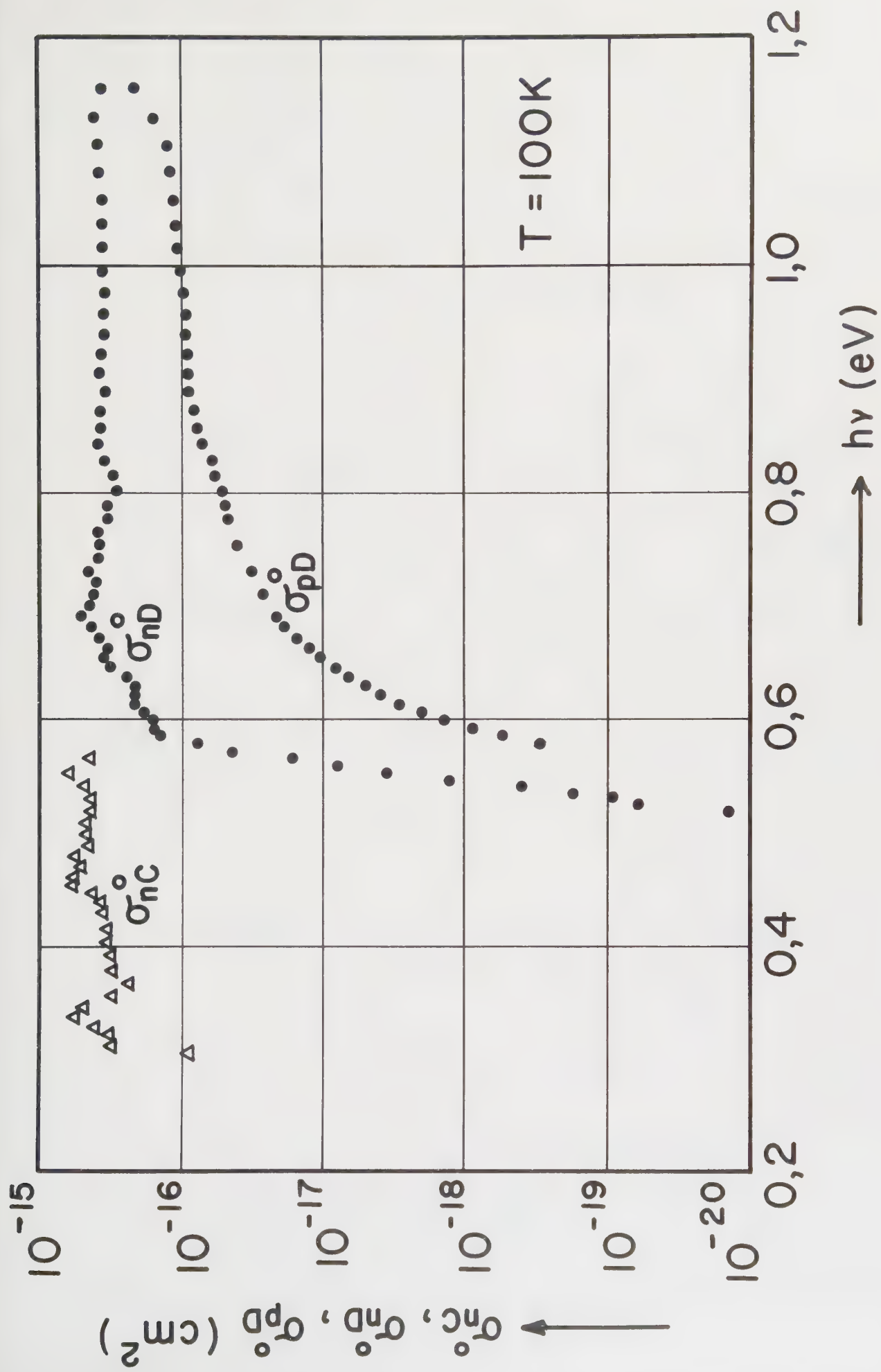
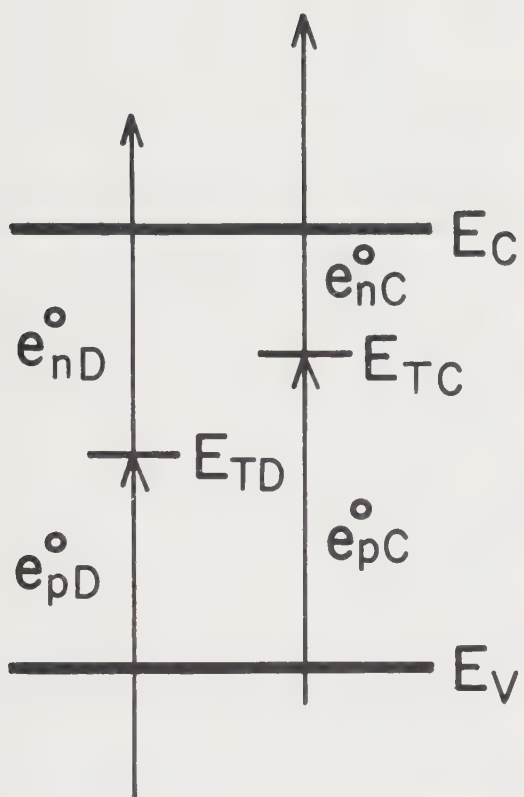
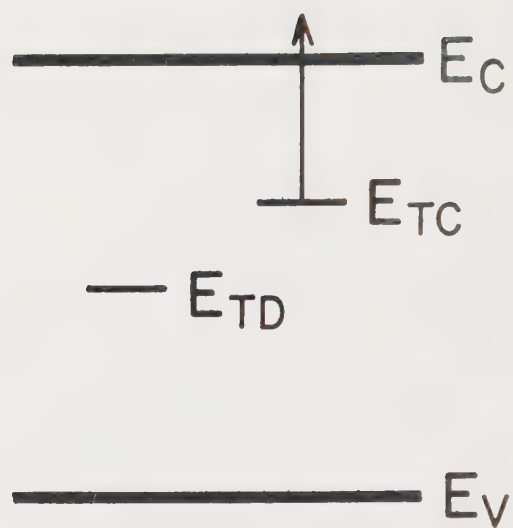


Fig.4



a)



b)

Fig.5

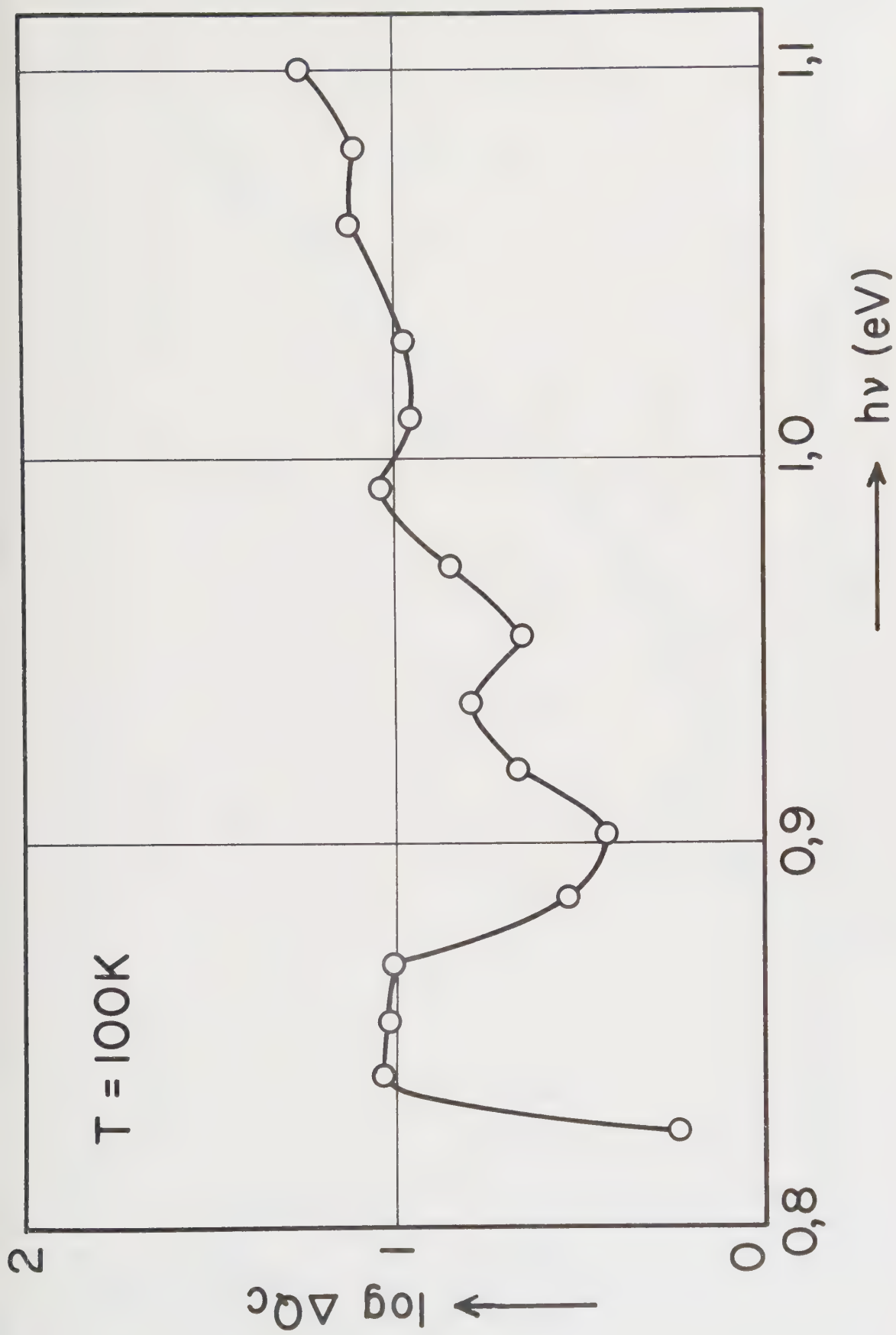


Fig.6

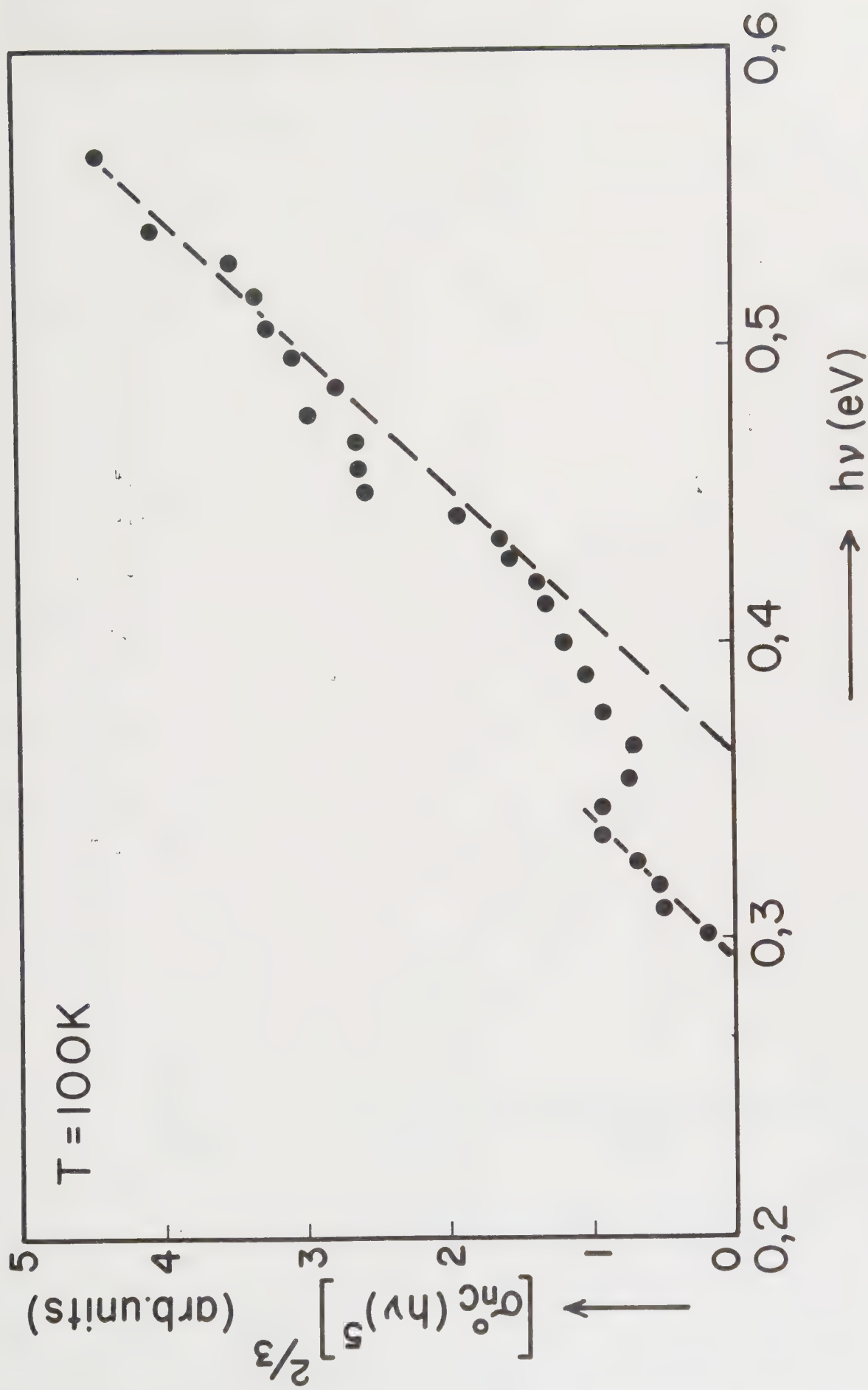


Fig.7

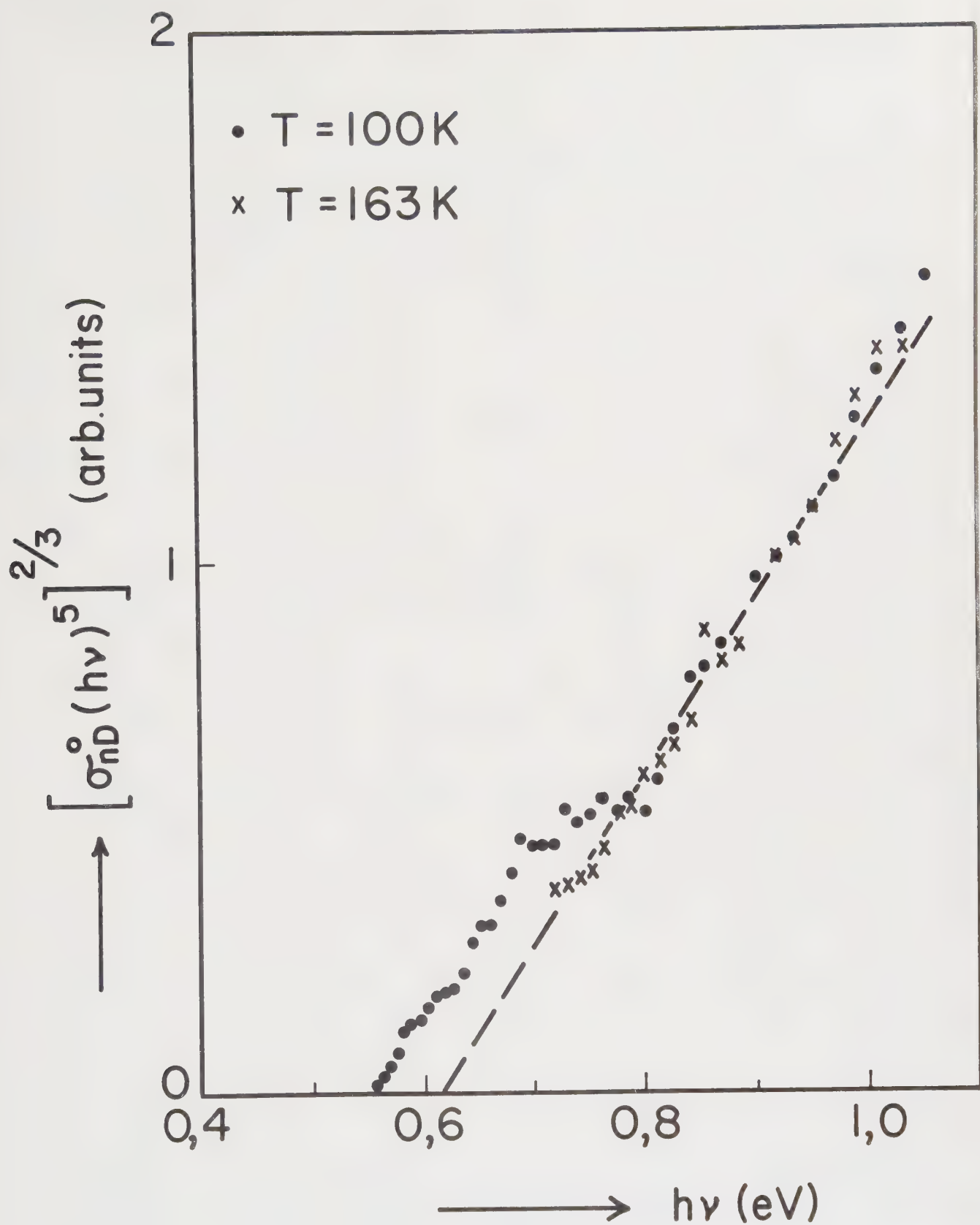


Fig. 8

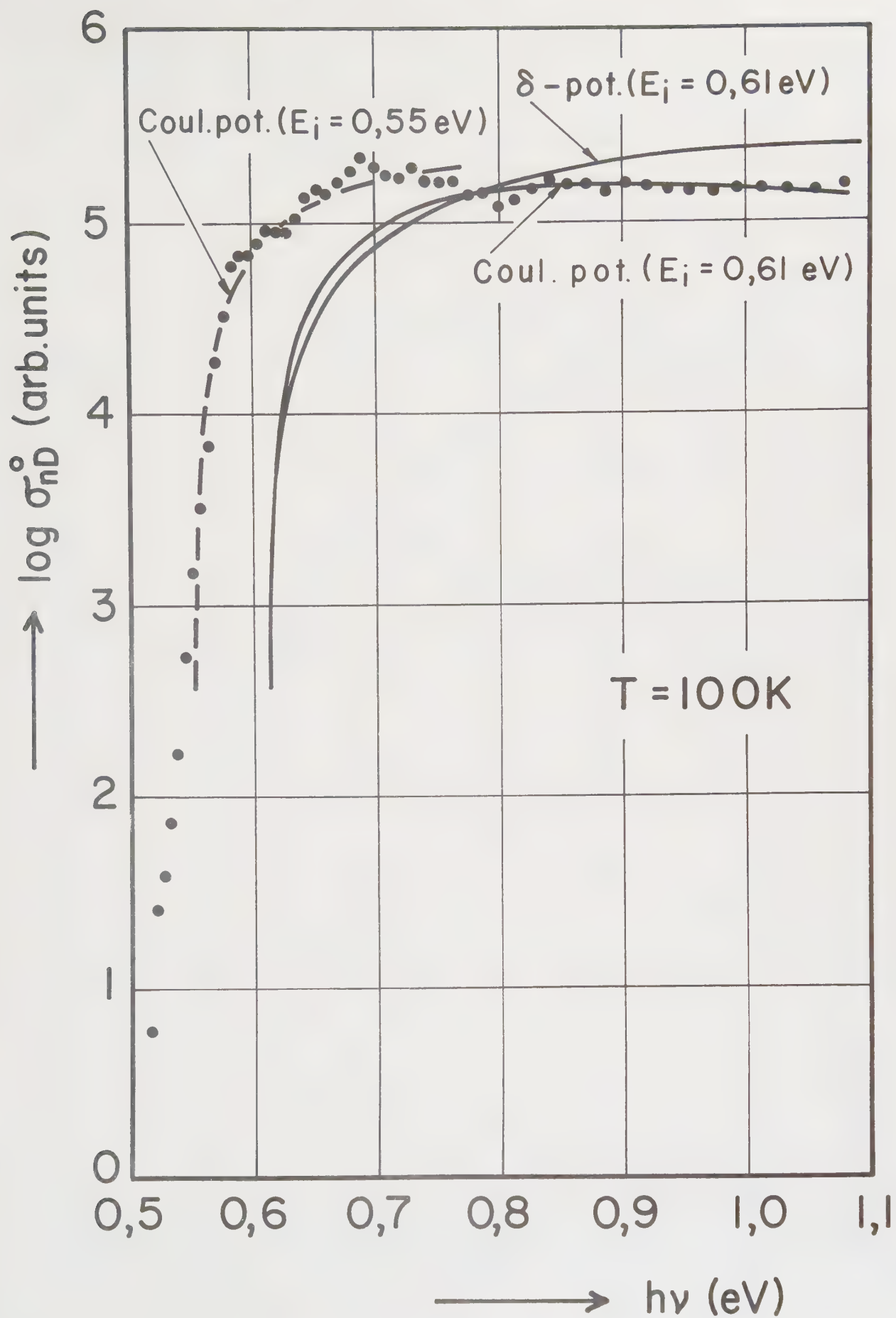


Fig.9

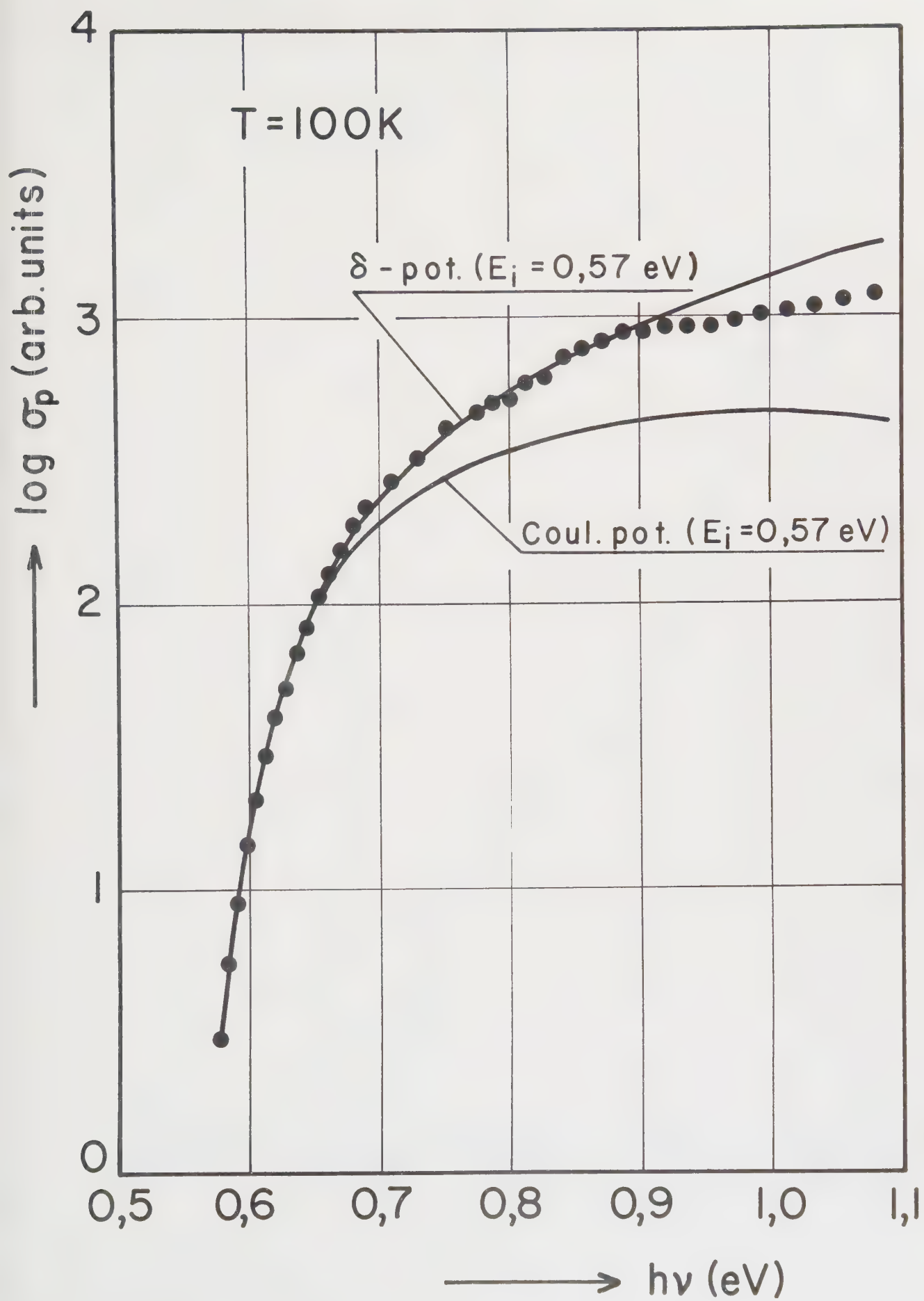


Fig.10

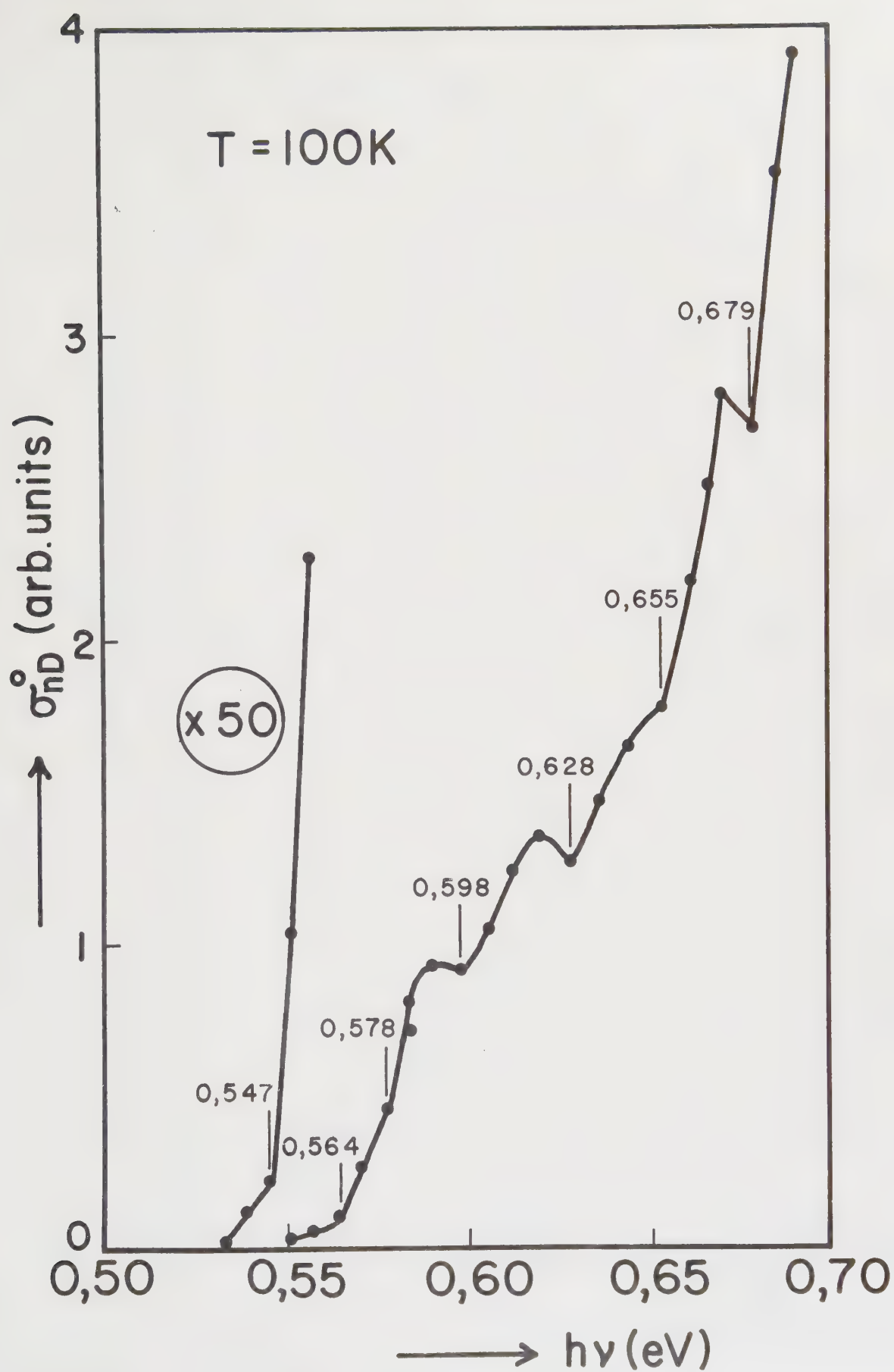


Fig. II

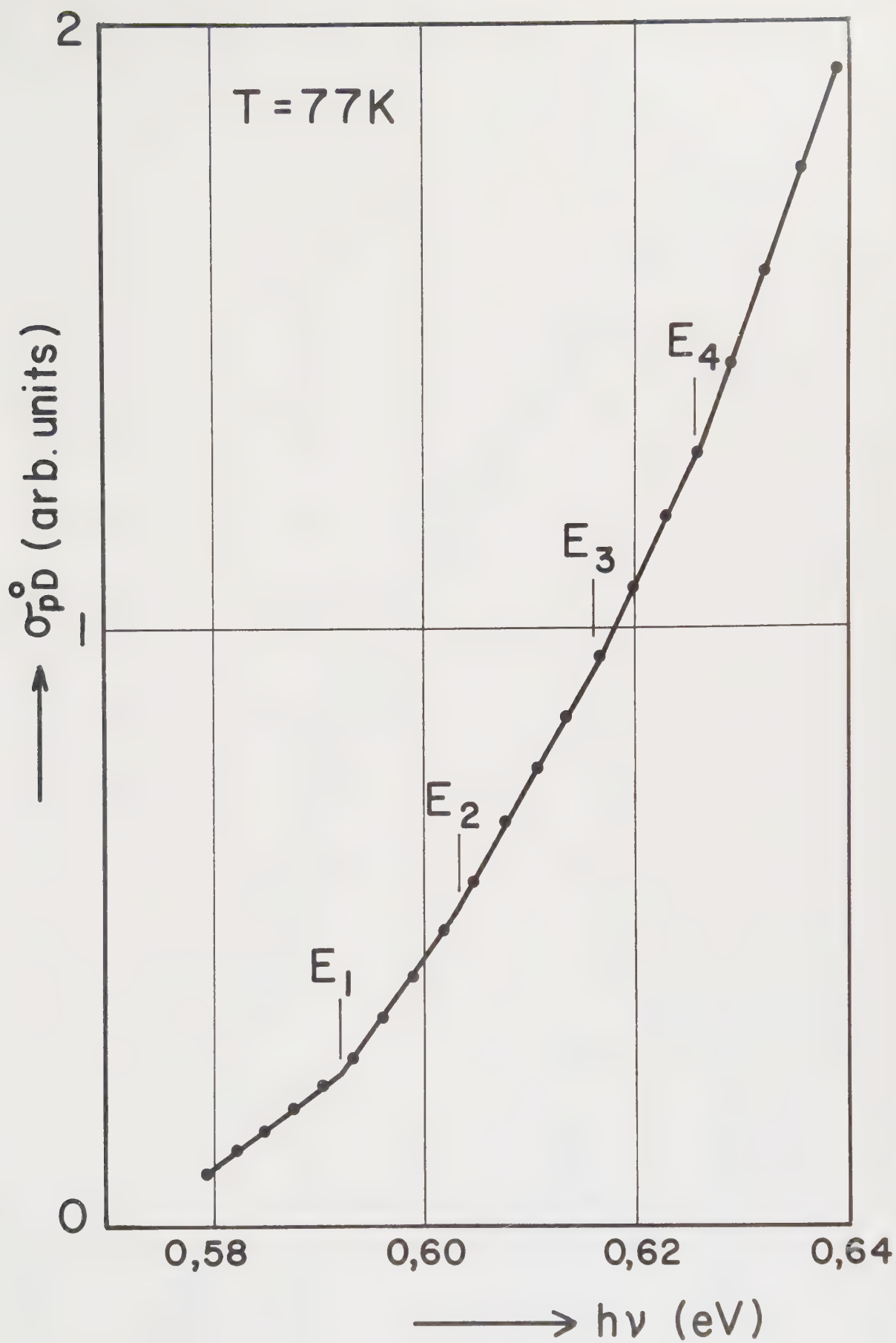


Fig. 12

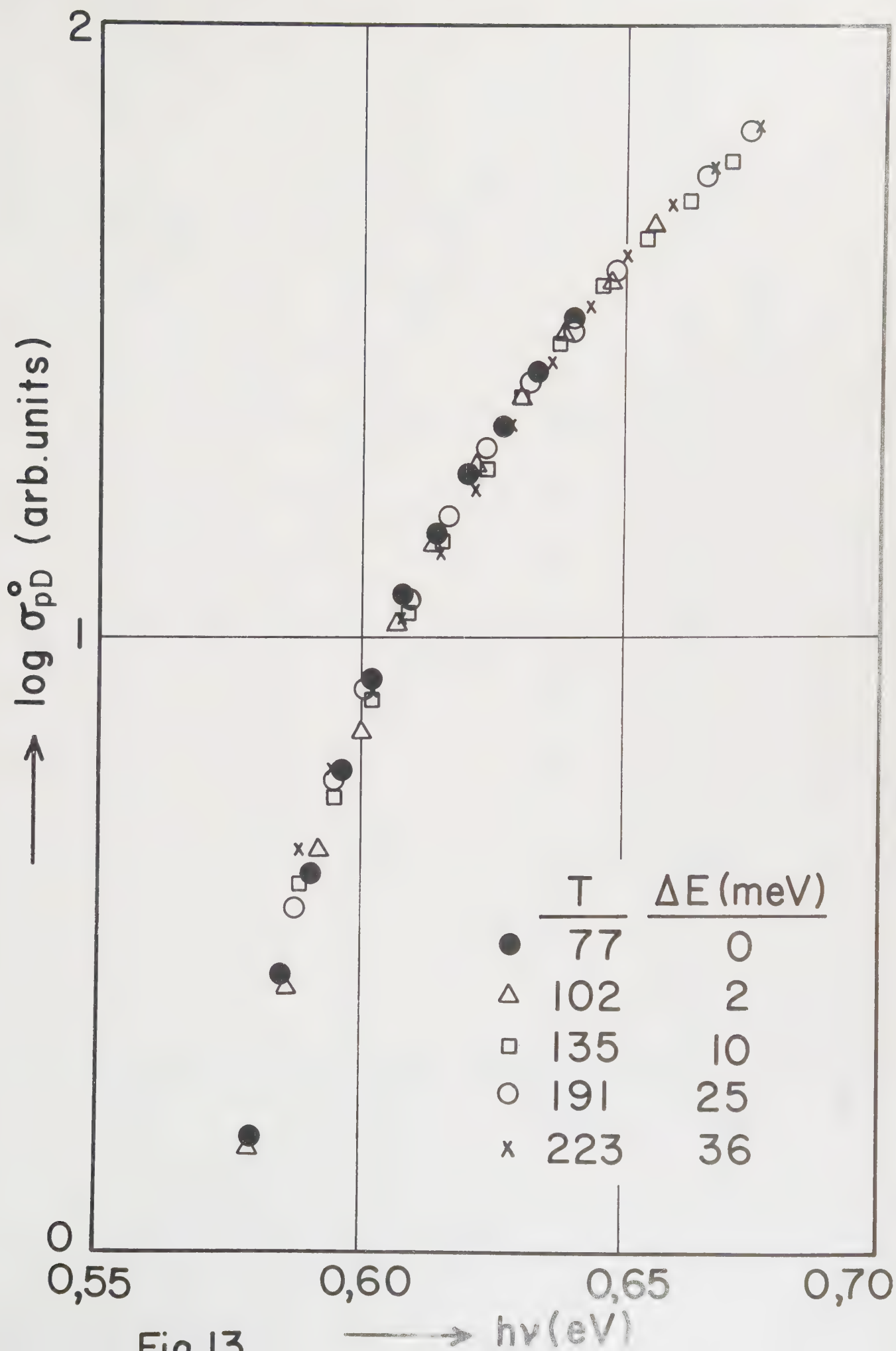


Fig 13

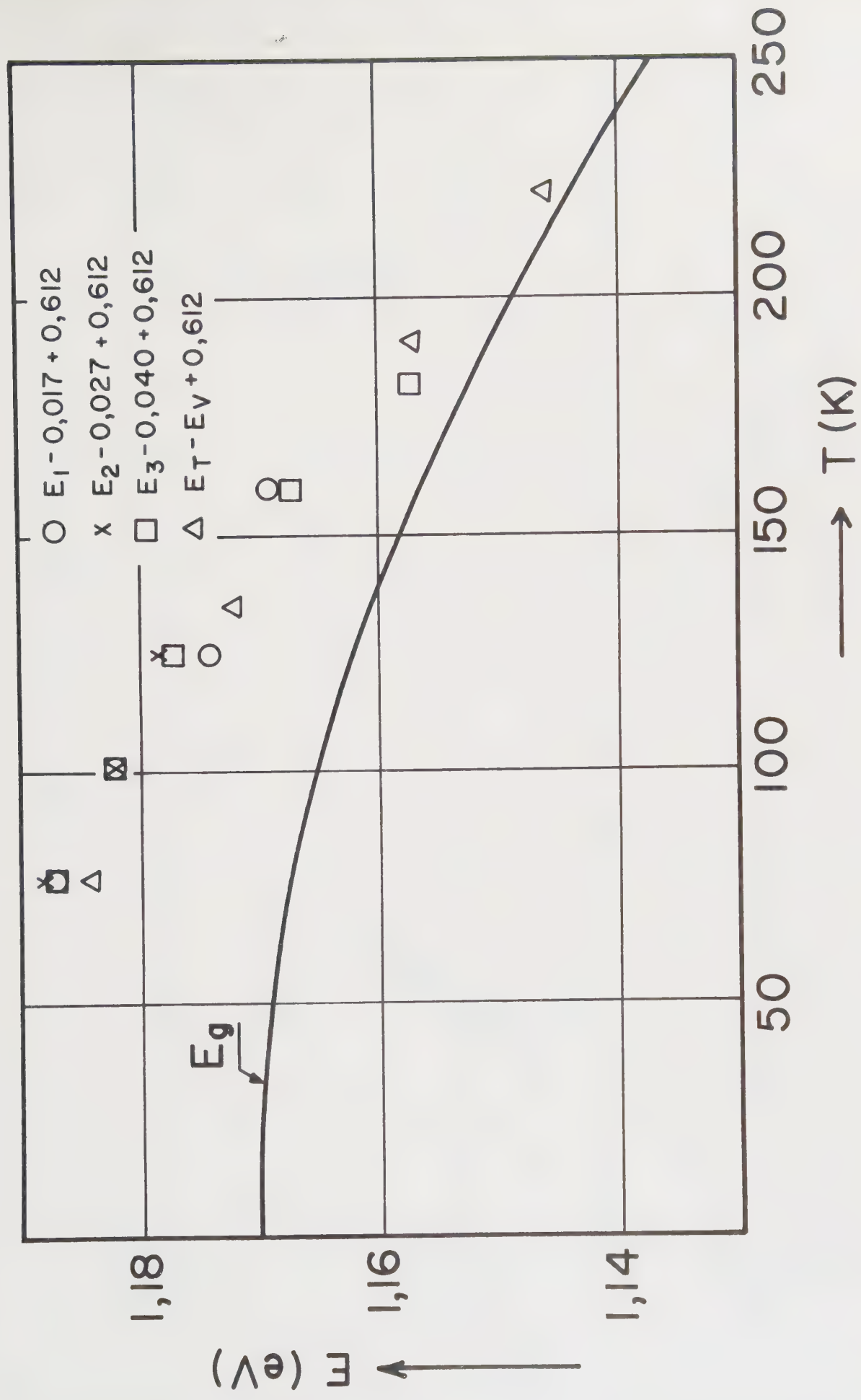


Fig.14

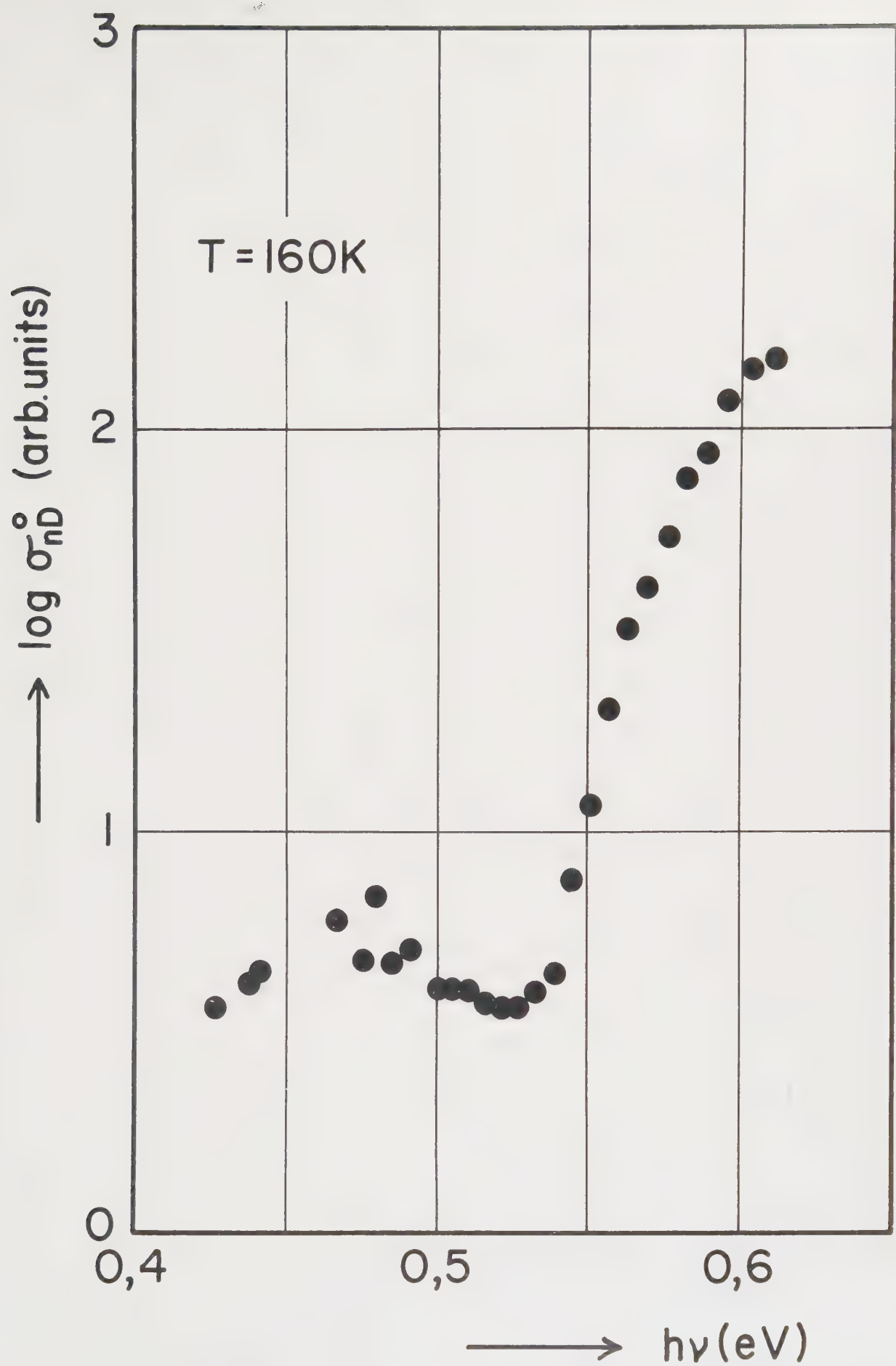


Fig.15

